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A Re-Evaluation of the Covalent Radii of Some of the Elements

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(Received November 11, 1946)

The Schomaker-Stevenson correction for ionic character, $-\beta|x_A-x_B|$, of the covalent radii additivity rule, $d_{AB}=r_A+r_B$, is extended to double bonds. The value of the parameter β found for these is 0.06. Several revisions in the table of covalent radii are proposed. The double-bond covalent radii of oxygen and nitrogen are chosen as 0.604A and 0.62A, respectively, or one-half the bond lengths of O_2 and of the $\diagdown N=N \diagup$ length in azomethane. The single- and double-bond covalent radii of carbon are revised upward to 0.79A and 0.675A to make them in accord with the lengths predicted by Mulliken, Rieke, and Brown for ideal single and double CC bonds. The newly assigned values are shown to be consistent with double bonds formed between unlike atoms when the shortening caused by ionic character is taken into account. Some other covalent radii are determined by extrapolation of curves determined by the known radii and by application of the revised additivity rule.

SCHOMAKER and Stevenson[1] have shown that the values of the single-bond covalent radii for N, O, and F in the Pauling-Huggins table[2] of covalent radii are significantly shorter than recent accurate measurements of the interatomic distances in H_4N_2, H_2O_2, and F_2 would indicate. They point out that the Pauling-Huggins values for nitrogen (0.70A) and oxygen (0.66A) were obtained from a curve drawn through the point for carbon (0.77A) and the point for fluorine (0.64A), and that the value used for fluorine was that obtained from the interatomic distance of F_2 in a state which is now known not to be the ground state. They accordingly proposed for the single-bond covalent radii of N, O, and F values of 0.74A, 0.74A, and 0.72A, respectively, or one-half the interatomic distances in hydrazine, hydrogen peroxide, and fluorine.[1]

In the same contribution Schomaker and Stevenson demonstrated the effects of ionic character on the interatomic distances between atoms of unlike electronegativity; they showed that the equation,

$$d_{AB}=r_A+r_B-\beta|x_A-x_B|, \qquad (1)$$

with $\beta=0.09$, can be used to predict approximately the length of single bonds, d_{AB}, between atoms of widely different electronegativities. Here r_A and r_B are the normal single-bond covalent radii, and x_A and x_B are the electronegativities of the atoms A and B. Thus, when x_A equals x_B and the bond has no ionic character, the equation reduces to the additivity rule. For bonds between atoms differing greatly in electronegativity the bond lengths are significantly shorter than the added sum of the covalent radii.

[1] V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. 63, 37 (1941).
[2] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), p. 164.

TABLE I. Calculated and observed interatomic distances of some double bonds.

Link	Interatomic distance: Observed	Calculated[a]	Sum of radii[b] (Pauling)
Be=O	1.331[c]	1.34	
>C=C<	1.35[d] 1.330[e]	(1.35)	(1.330)
>C=O	1.21[f] 1.22[g] 1.24[h]	1.225	(1.215)
>C=N<	1.26[i]	1.27	1.265
>C=S		1.61	1.605
>N=N<	1.24[j]	(1.24)	1.20
>N=O	1.22[k]	1.20	1.15
O=O	1.208[c]	(1.208)	1.10
S=O	1.494[c]	1.49	1.49
S=S	1.89[c]	(1.88)	(1.88)
Se=O		1.62	1.63
Se=Se	2.16[c]	(2.16)	(2.16)

[a] $d_{calc}=r_A+r_B-0.06|x_A-x_B|$, with r_A and r_B the revised double-bond covalent radii of Table II.
[b] $d'=r_A'+r_B'$, with r_A' and r_B' the Pauling double-bond covalent radii values. Reference 2.
[c] Reference 4.
[d] For ideal or pure C=C double bond, see reference 10.
[e] For CC bond in ethylene which has 12 percent triple-bond character, E. H. Eyster, J. Chem. Phys. **6**, 580 (1939).
[f] For >C=O bond in formaldehyde, D. P. Stevenson, J. E. LuValle, and V. Schomaker, J. Am. Chem. Soc. **61**, 2508 (1939).
[g] For >C=O bond in acetaldehyde, D. P. Stevenson, H. D. Burnham, and V. Schomaker, J. Am. Chem. Soc. **61**, 2922 (1939).
[h] For >C=O bond in thio-acetic acid, W. Gordy, J. Chem. Phys. **14**, 560 (1946); also for C=O of the formic acid monomer, J. Karle and L. O. Brockway, J. Am. Chem. Soc. **66**, 574 (1944).
[i] This value for the C=N double bond length has been indirectly deduced from x-ray diffraction data on dicyandiamide by E. W. Hughes, J. Am. Chem. Soc. **62**, 1258 (1940).
[j] See reference 9.
[k] For >N=O of methyl nitrite, G. W. Wheland, *The Theory of Resonance* (John Wiley and Sons, Inc., New York, 1944), p. 287. This bond is probably slightly longer than a pure N=O bond would be because of possible resonance of the normal structure, $CH_3-O-N=O$ with $CH_3-O^+=N-O^-$.

For example, the sum of the single-bond covalent radii of C and F in methyl fluoride is 1.51A, whereas the Schomaker-Stevenson rule gives 1.38A, close to the measured value,[3] 1.396A.

EXTENSION OF THE SCHOMAKER-STEVENSON RULE TO DOUBLE BONDS

Schomaker and Stevenson did not treat cases involving double bonds. However, from the marked effects of ionic character on the single-bond lengths one might expect significant, though somewhat less pronounced, shortening of a double bond caused by ionic character. This is especially true of the first period elements where double bonds can be formed between atoms differing greatly in electronegativity.

With some degree of success I have extended the Schomaker-Stevenson rule to double bonds by determining empirically the value of the constant β which best applies to them. The value found for β, 0.06, is slightly more than one-half that, 0.09, which applies to single bonds. The equation

$$d_{AB}=r_A+r_B-0.06|x_A-x_B| \qquad (2)$$

was found to apply satisfactorily to the few cases for which sufficient data were available for comparison. The results are shown in Table I. The values of r_A and r_B, double-bond covalent radii for the first period elements, are the revised values discussed below and listed in Table II. The double-bond radius used for sulfur is 0.94A, or one-half the bond length[4] in S_2; that used for selenium is 1.08A, one-half the bond length[4] in Se_2. The electronegativity values are listed in the third column of Table I. That for sulfur is 2.53, and that for selenium is 2.4. Electronegativity values for these and many other elements are compiled elsewhere.[5]

SOME PROPOSED REVISIONS IN THE TABLE[2] OF COVALENT RADII

Since the values for the double-bond covalent radii as given by Pauling[2] were in some instances

TABLE II. Covalent radii and electronegativities of first period elements.[a]

	Be	B	C	N	O	F
Single-bond radius		— (0.88)	0.79 (0.771)	0.74[b] (0.70)	0.73 (0.66)	0.72[b] (0.64)
Double-bond radius	0.86	— (0.76)	0.675 (0.665)	0.62 (0.60)	0.604 (0.55)	0.60 (0.54)
Triple-bond radius		— (0.68)	— (0.602)	— (0.547)	0.53 (0.50)	
Electronegativity	1.45	1.9	2.55	2.98	3.45	3.95

[a] The values given in parentheses are those compiled by Pauling, reference 2. A dash is placed where no change from these values seemed justified.
[b] A Schomaker-Stevenson value, reference 1.

[3] D. M. Dennison, Rev. Mod. Phys. **12**, 175 (1940).

[4] G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice Hall, Inc., New York, 1939), p. 483.

[5] W. Gordy, Phys. Rev. **69**, 604 (1946); also reference 2, p. 64.

determined by the application of the straight additivity rule to double bonds having considerable ionic character, it was necessary to revise some of his values before the Schomaker-Stevenson rule could be satisfactorily adapted to double bonds. New values for the first period elements, including some by Schomaker and Stevenson, are given in Table II, with the Pauling values for comparison.

Oxygen

For the double-bond covalent radius of oxygen I have chosen 0.604A, or one-half the accurately measured bond distance[4] in O_2. This is not a new proposal as Sidgwick[6] several years ago assigned 0.60A as the double-bond radius of oxygen. However, the value more recently determined by Pauling[2] from $\rangle C=O$ bonds, 0.55A, is 9 percent lower. The ground state of O_2 is known to be a $^3\Sigma_g^-$ state.[4] Pauling[7] describes its bond as composed of a single electron-pair plus two three-electron bonds. This combination, he points out, is about equivalent in energy to the double-bond state. According to the molecular orbital theory there would be four more bonding than antibonding electrons in O_2, and its bond may be regarded as a double one. The ground state[4] of S_2 is also a $^3\Sigma_g^-$; and Pauling[2] has assigned for the double-bond covalent radius of S a value which is essentially one-half the interatomic distance in this molecule. That the oxygen radius determined from O_2 cannot be added to the double-bond carbon radius to give the $\rangle C=O$ length in acetaldehyde, for example, appears to be caused by the large difference in the electronegativity of C and O rather than by $^3\Sigma_g^-$ ground state* of O_2.

To obtain the triple-bond radius listed for oxygen, I have merely extended the lower curve of Fig. 1. Since oxygen does not form a pure triple bond, the value obtained has no physical counterpart. Nevertheless, it may be useful in discussing bonds having some triple-bond character, as, for example, that of carbon monoxide.

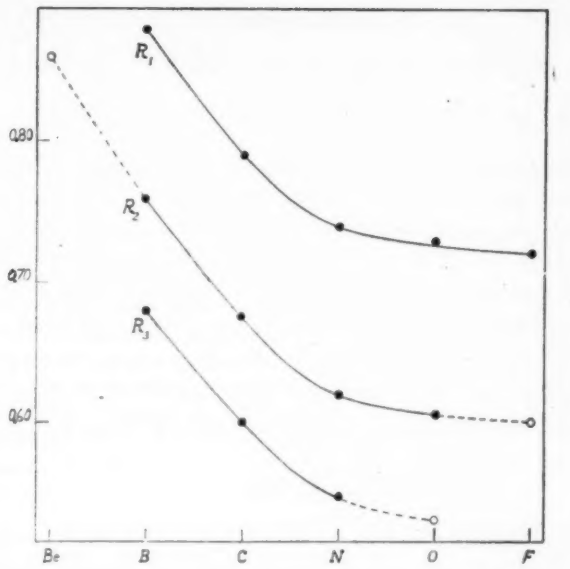
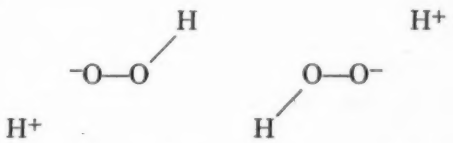


FIG. 1. A plot of covalent radii of first period elements. Top curve, R_1, for single-bond covalent radii; middle curve, R_2, for double-bond covalent radii; bottom curve, R_3, for triple-bond covalent radii.

Because the value of the single-bond covalent radius given by Schomaker and Stevenson[1] for oxygen, 0.74A, does not lie on the smooth curve (top curve of Fig. 1) determined by the other first period elements, I have listed the value determined by this curve, 0.73A, for the oxygen single-bond radius. This value is still within the possible experimental error of one-half the measured O—O distance in H_2O_2 and is exactly one-half that measured by x-ray diffraction of O—O in urea-hydrogen peroxide.[8] Resonance of the types



may increase slightly the O—O distance in hydrogen peroxide over that expected for an ideal O—O single covalent bond. Similar resonance would occur in hydrazine, but it would be less than that in H_2O_2 because of the lower electronegativity of N as compared to O.

[6] N. V. Sidgwick, *The Covalent Link in Chemistry* (Cornell University Press, Ithaca, New York, 1933), p. 85.
[7] L. Pauling, reference 2, p. 273.
* The interatomic distance for the singlet state, $^1\Sigma_u^-$, is 1.223A (W. Jevons, "Band spectra of diatomic molecules," Phys. Soc. London, p. 290, 1932), which leads to a value for the double-bond radius of oxygen 0.611, close to that determined by the $^3\Sigma_g^-$ state.

[8] C. Lu, E. W. Hughes, and P. A. Giguère, J. Am. Chem. Soc. **63**, 1507 (1941).

Nitrogen

The double-bond covalent radius chosen for N is one-half the $\diagdown N=N \diagdown$ bond distance in azomethane,[9] 1.24A. This value, however, has not been measured accurately; and in the choice of the value as 0.62A, first consideration was given to its being the value obtained by drawing a smooth curve through the points determined by carbon (0.675A) and oxygen (0.604A), and to the symmetry of this curve with the corresponding ones for the single and triple radii of the first period elements. These curves are shown in Fig. 1.

Carbon

Though Pauling's values for both single and double-bond carbon covalent radii were selected from CC bonds and hence are not subject to error caused by ionic character, the CC single and double bonds used to determine these radii have since been shown by Mulliken, Rieke, and Brown[10] to have 11 percent double-bond character and 12 percent triple-bond character, respectively. I have accordingly listed for the carbon radii one-half the lengths predicted by Mulliken, Rieke, and Brown for an ideal single (1.58A) and an ideal double (1.35A) CC bond.

[9] L. R. Maxwell, J. Opt. Soc. Am. **30**, 374 (1940). This is also the length of the $\diagdown N=N\equiv$ bond in methyl azide, L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **59**, 13 (1937).

[10] R. S. Mulliken, C. A. Rieke, and W. G. Brown, J. Am. Chem. Soc. **63**, 41 (1941).

Beryllium

The beryllium double-bond radius, 0.86A, was obtained by extrapolation of the smooth curve for double-bond covalent radii of the first period elements shown in Fig. 1. The value obtained in this way gives satisfactory agreement when used in relation (2) to predict the interatomic distance in BeO. See Table I.

Fluorine

The revised value, 0.60A, for double-bond r_F was obtained by extrapolation of the middle curve of Fig. 1.

Calcium, Strontium, and Barium

Very approximate predictions of the double-bond covalent radii of these elements can be made with Eq. (2) from the measured interatomic distances[4] in CaO, SrO, and BaO, assuming of course that double bonds exist in these molecules. The results obtained in this way are 1.29A for Ca, 1.36A for Sr, and 1.35A for Ba.

EFFECTS OF IONIC CHARACTER ON TRIPLE-BOND LENGTHS

From a comparison with the value of the constant β in Eq. (1) for single and for double bonds, one may expect the Schomaker-Stevenson rule to hold for triple bonds with a value for β about 0.03 or 0.04. However, there are not enough sufficiently accurate data available on pure triple bonds to test the relation.

The Asymmetric Rotor. IV. An Analysis of the 8.5-μ Band of D_2O by Punched-Card Techniques

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(Received October 25, 1946)

An analysis of the 8.5-μ band of D_2O has been made by matching the observed transmission curve (published by Barker and Sleator) with a calculated curve. This was obtained by punched-card techniques developed for analyzing incompletely resolved spectra, in which the relative intensity and position of every line was computed by rigid-rotor theory for various choices of moments of inertia, and the absorption coefficients summed over a suitable "slit width." The band is caused by a transition in which the induced electric moment is parallel to the intermediate axis of inertia. Its center is at 1179 cm^{-1}. The most satisfactory fit was obtained with moments calculated by the empirical equation of Fuson, Randall, and Dennison which applies an isotope effect to the known moments of inertia of H_2O, corrected slightly for the known values of $\Delta = I_C - I_B - I_A$. The reciprocal moments are 15.38, 7.25, and 4.84 cm^{-1} for the ground state, and 16.50, 7.33, and 4.79 cm^{-1} for the upper state (the first deformation vibrational level).

INTRODUCTION

IN a previous paper[1] we have described a method, based on punched-card procedures, of analyzing band spectra of asymmetric rotors. The principle was to calculate the position and absorption coefficient of every line appearing in the band, and to sum the coefficients over appropriate slit widths. Trial-and-error procedures result in the determination of a set of moments for the upper and lower states. It was anticipated that this approach could yield effective moments of inertia even when the band was incompletely resolved.

Even with machine methods, the number of trials needed to determine the seven molecular constants is large. In order to investigate the possibilities of this approach, it has been first tried on the 8.5-μ band of D_2O. No vibrational-rotational bands of D_2O have hitherto been analyzed, so that the determination of moments of inertia in a vibrational state will be of interest in the theory of this molecule. This band is also suitable for an initial approach because the moments of the lower state are known exactly, and those of the upper state can be predicted by an empirical theory. With these constants known at least fairly closely, other questions in such analyses could be studied. For example, the analysis[2] of the pure rotation spectrum of D_2O has shown that some of the rotational energy levels depart very greatly from those of the rigid rotor, chiefly on account of centrifugal distortion. There is, therefore, a question of whether our procedure is valid as long as it is based on the tables of reduced energy levels of rigid rotors. Another question is whether deviations from Beer's law, on account of the large number of lines of varying absorption coefficient in each slit width, would depend so much on the experimental conditions of source of radiation, slit width and shape, resolving power of the instrument, etc., as to invalidate the procedure.

ROTATIONAL LEVELS OF D_2O

A hitherto unanalyzed, incompletely resolved band of D_2O at 8.5μ has been reported by Barker and Sleator.[3] Unfortunately, the percentage transmissions were not given. However, the positions of the major peaks were measured accurately, and a graph given including subsidiary peaks. The richness of this spectrum in sharply defined peaks suggests that the moments of inertia of the two levels involved might be found by our procedure. Since the theory of distortion of the rigid-rotor levels is not adapted to our procedure, the position of the lines has been calculated on the basis of the rigid-rotor levels of both states. Although the term values of the rotational levels of the lower state are

[1] G. W. King, P. C. Cross, and G. B. Thomas, J. Chem. Phys. **14**, 35 (1946).
[2] N. Fuson, H. M. Randall, and D. M. Dennison, Phys. Rev. **56**, 982 (1939).
[3] E. F. Barker and W. W. Sleator, J. Chem. Phys. **3**, 660 (1935).

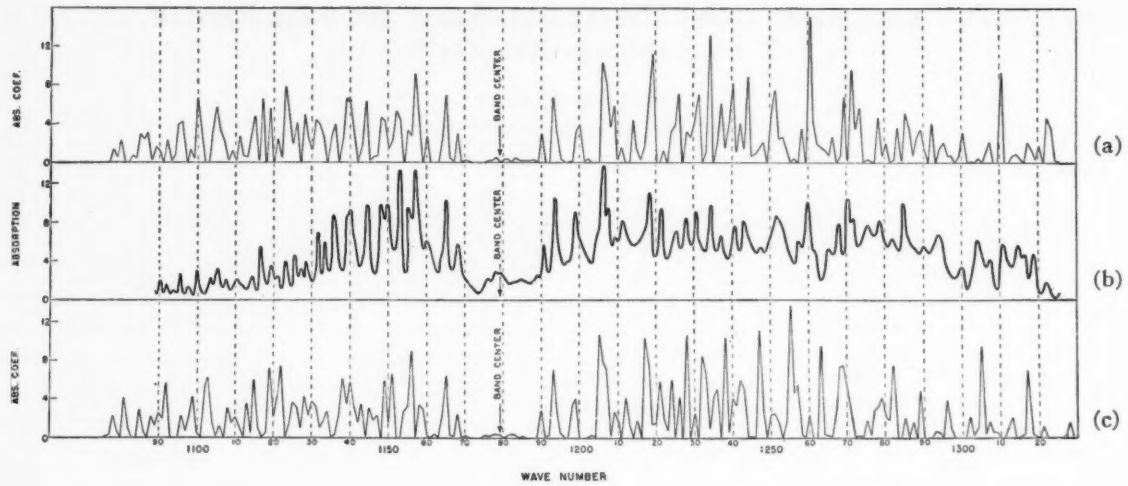

FIG. 1. The middle curve is replotted from the table and curve given by Barker and Sleator (reference 3). The upper curve is based on the calculated moments, columns 2 and 7 of Table I. The adjusted moments in columns 3 and 8 give practically the same curve. The lower curve is calculated from the upper-state moments in column 5. The vertical scale is arbitrary in all cases.

known, they were not used because the corrections applied to upper and lower states largely cancel. Furthermore, the important lines in this band arise from levels of low K_{-1} (or τ) value where the amount of distortion is small in any case. For the lower state the effective reciprocal moments chosen by Fuson, Dennison, and Randall were used, namely 15.38, 7.25, and 4.83 cm^{-1} (corresponding to moments 1.820, 3.860, and 5.794×10^{-40} gcm^2). For the upper state, the formulas given by these authors for computing the isotope effect on the anharmonicity coefficients in the known expressions for the moments of inertia of H_2O were used. The predicted reciprocal moments for the first deformation vibrational level, the upper state of the 8.5-μ band, are accordingly 16.50, 7.33, and 4.77 cm^{-1} (corresponding to moments 1.696, 3.818, and 5.867×10^{-40} gcm^2).

RESULTS

With these constants, the procedure described in reference 1 was followed, with arbitrary band center. The absorption coefficients were summed over various slit widths. A slit width of 1 cm^{-1} was found to be appropriate, and the sums of the absorption coefficients over this interval were plotted for several choices of moments of inertia of the upper state. The calculations were done for transition probabilities appropriate to both a- and b-type bands, where the induced moment is parallel to the axis of the least and intermediate moment of inertia, respectively. There is no doubt this is a b-type band. Because numerical values of the percent transmission are not available, further determination of slit width and shape to fit the experimental curve better were not made. Investigation of this point for other bands of this general structure indicate that the relative intensities would not be modified seriously by such considerations.

The experimental curve is shown in Fig. 1(b). This was drawn from the table of position of the principal peaks and careful measurement of the curve given by Barker and Sleator. The curve for the moments based on the isotope effect on H_2O moments (given above and in columns 2 and 7 of Table I) is shown in Fig. 1(a). It agrees surprisingly well with the experimental, considering the fact that deviations from the rigid rotor and from Beer's law were not incorporated. By superposition of the calculated and observed curve the band center was located at 1179 cm^{-1}.

In order to test the sensitivity of the calculated curve to changes in the moment, other moments (given in Table I) were tried. The set in column 4 was one of the early approximations and gave a curve with some of the features of the experimental curve (especially in the center),

but the agreement was by no means as satisfactory as that of Fig. 1(a).

During the course of this work, Dickey and Nielsen[4] reported the re-measurement of this band with a grating, and gave effective moments for the upper state listed in column 5 of Table I. Naturally, these moments were tried by our procedure. The resulting curve is given in Fig. 1(c). The over-all agreement is not as good as with the predicted moments of column 7. We believe the reason for the disagreement of the moments in column 5 is that, although those moments were obtained from a better resolved spectrum, they were based only on levels of low J. Our experience in analyzing these spectra is that moments based on the low levels, although easy to calculate, are subject to large errors, and that better approximations to effective moments can be made on the basis of lines involving high J values, or as in the procedure used here, on all the lines involved. The reason is that the term values for low J have one or two less significant figures than those of high J. For example, the peaks in the center of the band can be fitted by any of the moments in Table I equally well. It could be argued that this is offset by distortion increasing with J. However, we can define the effective moments as those fitting the lowest τ levels at all J values, and since the peaks in this type of spectrum arise from these levels (chiefly because they have large Boltzmann factors), the moments derived by our analysis are effective moments, defined as forming a framework of rigid-rotor levels to which could be added the elaborations of centrifugal and vibrational interactions.

Subsequently Dickey and Nielsen changed[5] the moments given in the original abstract to values close to ours (Table I, column 6). The higher value of c does not fit the data quite as well as that in column 7, but the data available to us is possibly not suitable for making a decision. There is, however, another criterion which has to be met. Darling and Dennison[6] have shown that in molecules of this type the discrepancy Δ in moments of inertia, which would be zero if the molecule was rigid, can be expressed as

$$\Delta = I_C - I_B - I_A = (h/\pi^2 c)[\omega_3^2(\omega_2(\omega_3^2-\omega_2^2))^{-1}(n_2+\tfrac{1}{2}) - \omega_2^2(\omega_3(\omega_3^2-\omega_2^2))^{-1}(n_3+\tfrac{1}{2})], \quad (1)$$

where ω_2 and ω_3 are the vibrational frequencies at zero-point energy, which for D_2O are 1210.25 and 2883.79 cm^{-1}, respectively. Thus, it is possible to calculate Δ for any vibrational level of D_2O precisely.

$$\Delta = 0.2245(n_2+\tfrac{1}{2}) - 0.016(n_3+\tfrac{1}{2}). \quad (2)$$

For the ground state, the calculated Δ is 0.105 whereas the value corresponding to moments used by Fuson, Randall, and Dennison is 0.115. For the upper state, Δ should be 0.329, whereas the moments calculated by the empirical isotope effect equations give 0.353. These discrepancies are caused by the fact that the isotope effect is applied to the equations expressing the reciprocal moments as linear functions of the vibrational quantum number, which are not algebraically equivalent to those for the moments themselves, and hence of Δ. A more exact derivation of the

TABLE I. Summary of constants investigated for D_2O: The moments of inertia are I_A, I_B, and I_C in units of 10^{-40} gcm², with discrepancy $\Delta = I_C - I_B - I_A$, calculated with a value of $h/8\pi^2c = 27.9865 \times 10^{-40}$ from the corresponding reciprocal moments a, b, c in cm^{-1}, of asymmetry $\kappa = (2b-a-c)/(a-c)$. Column 2 gives the effective moments of the ground state of D_2O, calculated in reference 2 from the isotope effect on those of H_2O. Column 7 gives moments similarly calculated for the first deformation vibrational level, which determine a curve (Fig. 1(a)) in good agreement with the observed (Fig. 1(b)). Column 4 gives trial moments used to show the sensitivity of the calculated curve to choice of moments. Column 5 gives moments first suggested by Dickey and Nielsen, reference 4, and results in Fig. 1(c). Column 6 gives the revised moments of Dickey and Nielsen. Columns 3 and 8 are the calculated moments revised to fit the theoretical values of Δ. They result in a curve indistinguishable from Fig. 1(a) (at this resolution).

	Ground state		Upper state				
(1)	F.R.D.[a] (2)	Adj. (3)	Trial (4)	D & N[b] (5)	D & N[c] (6)	Reference 2 (7)	Final (8)
I_A	1.820	1.820	1.696	1.730	1.685	1.696	1.696
I_B	3.860	3.860	3.635	3.830	3.807	3.818	3.818
I_C	5.794	5.784	5.867	5.95	5.775	5.867	5.843
Δ	0.114	0.104	0.536	0.390	0.283	0.353	0.329
a	15.38	15.38	16.50	16.18	16.61	16.50	16.50
b	7.25	7.25	7.70	7.31	7.35	7.33	7.33
c	4.83	4.84	4.77	4.70	4.85	4.77	4.79
κ	−0.541	−0.543	−0.5	−0.545	−0.575	−0.564	−0.566

[a] Reference 2.
[b] Reference 4.
[c] Reference 5.

[4] F. P. Dickey and H. H. Nielsen, Chicago Meeting of the American Physical Society, June 1946.
[5] F. P. Dickey and H. H. Nielsen, Phys. Rev. **70**, 109 (1946).
[6] B. T. Darling and D. M. Dennison, Phys. Rev. **57**, 128 (1940).

moments of D_2O from those of H_2O could be made by working out the equations of Darling and Dennison, but the data at hand do not warrant this.

The value of Δ for the upper state is brought into agreement with (2) if $c=4.79$ cm^{-1}. This is within the sensitivity of our method (at the resolution of the data), and the curve with this value of c is only very slightly different from Fig. 1(a). Thus, we believe the best values of the moments of D_2O in the upper state are those given in the last column of Table I.

It is of interest to point out that essentially the whole of this band can be accounted for by levels up to $J=12$ showing that the basic tables of reduced energy and line strengths[7] on which the calculations are constructed are adequate for bands of this type of molecule.

CONCLUSIONS

The agreement of the calculated curve, Fig. 1(a), with the observed, Fig. 1(b), shows that the effective moments of D_2O in the 8.5-μ band are close to the values given in the last column of Table I. The curves for slightly different moments, such as those in columns 4 and 5, are substantially different.

Although we have not yet worked out an objective criterion of "goodness of fit," on the basis of "topological" features, such as number and relative magnitude of the peaks, we estimate the possible error in a, b, and c (reciprocal moments) as 0.1, 0.05, and 0.02 cm^{-1}, respectively.

The agreement shows that the moments of D_2O in its upper vibrational states can probably be calculated with sufficient accuracy from the isotope effect on those of H_2O.

This investigation also shows that the incompletely resolved spectra can be analyzed by computing the position and intensity of every line present, and summing the absorption over a "slit width" which in turn can be deduced from the experimental curve.

Because of the lack of numerical values of the transmission in the data used, further attempts to match the observed curve were postponed until further experimental data for this band becomes available.

[7] G. W. King, R. M. Hainer, and P. C. Cross, J. Chem. Phys. **11**, 27 (1943); P. C. Cross, R. M. Hainer, and G. W. King, J. Chem. Phys. **12**, 210 (1944). Values of $E(\kappa)$ for $J=11$ and 12 are about to be published.

The Asymmetric Rotor. V. An Analysis of the 3.7-μ Band of H_2S by Punched-Card Techniques

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(Received October 25, 1946)

The H_2S band at 3.7μ described by Nielsen and Barker is interpreted as the R branch of band for which the induced moment is parallel to the least axis of inertia, between the ground state with moments of inertia determined by Cross and an upper state with moments 2.8_3, 3.1_0, and $6.0_2\times10^{-40}$ gcm² (reciprocal moments 9.90, 9.04, and 4.65 cm⁻¹, respectively). The band center is 2625 cm⁻¹. Punched-card methods were used to do the following calculations. The relative position and intensities of all the lines in the band are computed by the theory of the rigid rotor, their absorption coefficients α summed over an interval of 0.5 cm⁻¹, or ⅓ of the slit width to give $\Sigma\alpha$. These are converted to transmissions, $e^{-q\Sigma\alpha}$, where q is an adjustable parameter. The transmissions over a range of 5 intervals are combined with suitable weight factors (1, 2, 4, 2, 1) to give the transmission through a "slit" of finite resolution and half width of 1 cm⁻¹. This computed transmission curve is compared directly with the actual experimental observations. These calculations were made for several estimates of the moments until a satisfactory fit was obtained.

INTRODUCTION

A VERY peculiar band of H_2S has been reported[1] at 3.7μ. We believe we can identify it as half of a fundamental of the asymmetric vibrational frequency ν_σ, where the induced moment is parallel to the least axis of inertia. This is contrary to the interpretation given in reference 1 as a complete band with no Q branch associated with an induced moment parallel to the intermediate axis. We believe it is impossible to identify the recorded curve as a complete band of an asymmetric rotor. Furthermore, there are certain reasonable restrictions on the moments of inertia of H_2S in the infra-red to a range of values which cannot possibly give rise to a complete band of the shape recorded.

RANGE OF MOMENTS

From the combination band at 9911 cm⁻¹ Cross[2] has been able, by accounting for all the lines of a completely resolved spectrogram, to determine the effective moments of inertia of the ground state and of the level $n_\sigma=1$, $n_\pi=3$, $n_\delta=0$. This gives the orders of magnitude of the moments of inertia of H_2S and of their dependence on the three vibrational quantum numbers. These trends in the moments are supported by an approximate analysis of the 2.6-μ band for which the data is also given in reference 1. A complete analysis of this band cannot be given at this time because of the more serious lack of resolution, although the principal features can be accounted for by moments $I_A=2.6_9$, $I_B=3.6_5$, and $I_C=6.0_6\times10^{-40}$ gcm². Fourteen sets of estimates of the moments have been tried, and we feel that the correct values cannot be far from those given.

Thus the moments obtaining in the upper level of the 3.7μ are fairly well prescribed. Furthermore, the three moments are not independent parameters, for Darling and Dennison[3] have shown that although $I_C-I_B-I_A=\Delta$ is not zero (as it would be for a rigid planar molecule), nevertheless it is dependent only on two parameters, $\Delta=k_\delta(n_\delta+\frac{1}{2})-k_\sigma(n_\sigma+\frac{1}{2})$. The coefficient of $n_\pi+\frac{1}{2}$ is extremely small for this type of molecule. Now k_σ and k_δ can be estimated from the fundamental frequencies, giving 0.231 and 0.025, respectively. Conversely, since the moments of two states have been determined exactly by Cross, these coefficients can be evaluated empirically as 0.314 and 0.040, respectively. The difference between these pairs of values is caused by the fact that the frequencies we have used in the expression for Δ given by Darling and Dennison were

[1] H. H. Nielsen and E. F. Barker, Phys. Rev. **37**, 727 (1931). The absorption curve in this paper has been redrawn in Fig. 1. A. D. Sprague and H. H. Nielsen, J. Chem. Phys. **5**, 85 (1937), state that this band was re-measured, with the same results as given in the first paper. This problem has recently been discussed with Professor Nielsen. The absence of absorption in the "P" and "Q" region has again been asserted by R. H. Noble and H. H. Nielsen, Paper Z9 of the programme of the New York Meeting of the American Physical Society, January, 1947.

[2] P. C. Cross, Phys. Rev. **46**, 536 (1934); *ibid.* **47**, 7 (1935); J. Chem. Phys. **5**, 370 (1937); P. C. Cross and B. L. Crawford, Jr., *ibid.* **5**, 371 (1937) and **5**, 621 (1937).

[3] B. T. Darling and D. M. Dennison, Phys. Rev. **57**, 128 (1940).

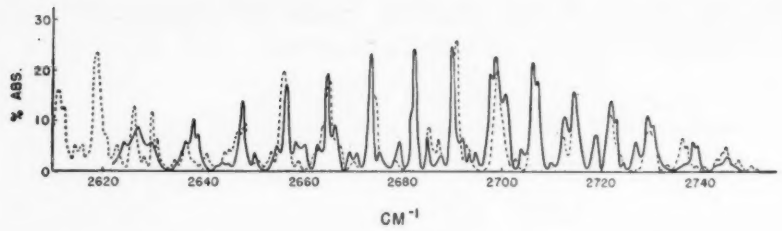

FIG. 1.

not corrected to equilibrium values, since band centers and anharmonicities are not yet known for H_2S.

The expression for Δ, with the two experimentally determined coefficients, thus enables us to calculate Δ for every vibrational state, and get a relation between I_C, I_B, and I_A, thus reducing the number of unknown parameters to two. This is of value not only in reducing the labor of the trial-and-error method, but of restricting the range of moments so that the appearance of the bands of a given molecule in the infra-red must fall into certain general types.

METHOD

The interpretation of the 3.7-μ band is based on a method[4] of analyzing partially resolved infrared spectra by taking into account all possible transitions, for a suitable range of possible values of the moments of inertia. The elaborate and extensive calculations are done by International Business Machine punched-card machines. In this stochastic method a series of estimates of these moments of inertia are made, from which all the rotational energy levels of both states are computed by means of the table[5] of the reduced energy levels (of the rigid rotor) for the chosen degree of asymmetry. From these the positions, ν, and absorption coefficients, α, of all lines are calculated, the latter based on the transition probabilities[6] of the asymmetric rotor and Boltzmann factors. Each line in the spectrum is represented by a card bearing its position and absorption coefficient.

The cards, i.e., lines, are arranged in increasing wave number ν, and α summed over various intervals corresponding to slit widths. A series of slit widths 0.5, 1, 2$\cdots$cm^{-1} are first tried, to find the order of magnitude of the one corresponding to the experimental data. Deviations from Beer's law can be allowed for in part by further elaborations made feasible by having the calculations on punched-cards. The absorption coefficients α are summed again over a fraction of the approximate slit width, and summary cards bearing $\sum\alpha$ prepared. Next transmissions, $e^{-q\sum\alpha}$, for each interval are obtained for each summation $\sum\alpha$ for several values of q, which is an unknown parameter involving the square of the induced dipole moment and the number of molecules in the path length. This was done by collation with a master set bearing x, $e^{-1.0x}$, $e^{-0.9x}\cdots e^{-0.1x}$, and a suitable shift of decimal point. The calculated total transmission (at approximately the experimental conditions of slit shape and width) at a given frequency, is calculated by adding to the transmission of the small interval at that frequency the transmissions of neighboring intervals on each side multiplied by weight factors, whose rate of decrease describes the slit shape and

TABLE I. Summary of constants of H_2S. The 3.7-μ band is between the ground state (000) whose constants were determined by Cross and the upper state (100). The constants for the (130) state found by Cross are given in the last column for comparison. Here I_A, I_B, and I_C are the moments of inertia in units of 10^{-40} gcm^2, with discrepancy $\Delta = I_C - I_A - I_B$; a, b, c are the corresponding reciprocal moments in units of cm^{-1}, with asymmetry $\kappa = (2b-a-c)/(a-c)$.

	State 000	100	130
I_A	2.693	2.82_7	2.824
I_B	3.096	3.09_5	3.340
I_C	5.926	6.01_9	6.261
Δ	0.137	0.097	0.097
a	10.393	9.90	9.910
b	9.040	9.04	8.379
c	4.723	4.65	4.470
κ	0.523	0.673	0.437

[4] G. W. King, P. C. Cross, and G. B. Thomas, J. Chem. Phys. **14**, 35 (1946).

[5] G. W. King, R. M. Hainer, and P. C. Cross, J. Chem. Phys. **11**, 27 (1943). This table of reduced energy levels has been extended to $J=11$ and 12, and now covers all the important levels appearing in this type of band.

[6] P. C. Cross, R. M. Hainer, and G. W. King, J. Chem. Phys. **12**, 210 (1944). By extrapolating the wings of the more important sub-branches, the small contribution of $J=13$ and 14 levels to the extreme ends of the bands were incorporated.

width. A few trials determine a "slit width and shape" equivalent to that obtaining in the experimental work, and also determine q. The small interval over which the α's were summed was 0.5 cm^{-1}, and the weighting factors were 1, 2, 4, 2, 1, so that the half-width was 1 cm^{-1}. A value of $q=0.053$ matched the height of most of the principal peaks. If the amount of gas in the light path had been measured, this value of q would have determined the magnitude of the induced dipole in this transition.

In this way a calculated transmission curve can be made and compared numerically with the observed percentage transmission. Successive estimates of the moments of inertia are made until a satisfactory fit with experiment is achieved.

RESULTS

It was found that the experimental curve of the 3.7-μ band of Nielsen and Barker can be reproduced quite well as the R branch of a band with induced moment parallel to the least axis of inertia, between the ground state with moments given by Cross,[2] and a vibrational state (100) with moments given in Table I. Curves for neighboring values of the moments were computed and give detectably poorer fits to the experimental data. On the basis of these, we estimate the uncertainties in a, b, and c are 0.03, 0.05, and 0.01 cm^{-1}, respectively. The band center is 2625 cm^{-1}.

DISCUSSION

The solid line in Fig. 1 is the experimental data given by Nielsen and Barker. The dotted curve is the calculated transmission curve obtained with the above moments, where it does not agree exactly with the experimental. The worst agreement is at the low wave number end, but this is where the observed absorption becomes zero instead of rising to the P branch, as predicted by the dotted curve.

It is our experience that the moments cannot be determined very accurately in this type of band in the absence of the absorption curve for the P branch, so that it did not seem worth while to try to fit the minor peaks in Fig. 1 any better. There seems to be no theoretical reason for the non-observance of the P branch. We hope to examine this infra-red band experimentally with a different type of spectrometer.

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An Experimental Contribution to the Problem of Diamond Synthesis

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Pressure up to 30,000 kg/cm², and in one case 45,000 kg/cm², has been applied to graphite alone, or to graphite seeded with diamonds, at temperatures above 2000°C. In order to maintain temperatures for times of the order of seconds it is necessary to make the apparatus large, a commercial 1000-ton press being used to generate the pressure. Two methods were used, external heating with rapid transfer of the heated specimen to the pressure vessel and application of pressure, and internal heating by a modified thermite reaction set off by the pressure itself. No detectable transformation of graphite to diamond was found in any of the experiments. In the experiments with internal heating it was established that the rate of inversion of diamond into graphite at a temperature above the melting point of molybdenum is a function of the pressure. The individual points are considerably scattered, but the mean points lie roughly on a straight line running from 100 percent graphitization at 15,000 kg/cm² to 0 percent at 30,000 kg/cm². Linear extrapolation would, therefore, indicate reversible transition from graphite to diamond at higher pressures. It has not been possible to check this by direct experiment. The graphite formed from diamond under these conditions has the same x-ray structure as ordinary graphite, indicating that there are no previously unknown modifications of graphite in the present range to complicate the problem. In an appendix the theoretical evidence is considered and the conclusion drawn that linear extrapolation of the equilibrium curve between graphite and diamond from data up to 1000°C gives too high values of pressure in a range above 2000° where the velocities become appreciable, and that the equilibrium curve more probably curves upward.

INTRODUCTION

IN order to achieve the transition from graphite to diamond, it is necessary not only to produce conditions such that the stability of diamond is higher than that of graphite as indicated by the thermodynamic potentials, but it is also necessary to reach temperatures so high that the transition will run with appreciable velocity. Within the last twenty-five years improved values of the thermodynamic parameters, in particular the heats of combustion, have revised previous estimates of the relative stability of diamond and graphite. At 0° absolute the discussion of Rossini and Jessup[1] indicates that the most probable pressure of reversible transition from graphite to diamond is 13,000 kg/cm². This pressure increases with increasing temperature at a rate depending on the thermodynamic parameters, in particular on specific heat and thermal expansion. I had found how to handle pressures of the order of magnitude of tens of thousands of kg/cm² as a matter of routine in the laboratory at room temperature, and had proved such pressures impotent to produce the transition,[2] which will not run at pressures as high even as 400,000 kg/cm². The controlling factor under ordinary conditions is, therefore, the velocity of transition. Judging by the known velocity of inversion of diamond into graphite at atmospheric pressure, temperatures of the general order of 2000°C or more would seem to be necessary if the transition is to run appreciably in the times available in the laboratory.

The natural method of attaining temperatures of this magnitude would be by internal electrical heating, and I did make various experiments with fine wires electrically heated within the pressure medium. The technical difficulties of any such method were evidently great, however, both because of the greatly enhanced thermal conductivity of ordinary substances under high pressure and because of increased chemical reactivity at high temperatures. Although methods of electrically heating the specimen *in situ* in the pressure vessel doubtless are not ruled out, it seemed to me that other methods, such as external heating, rapid transfer to the pressure vessel and rapid application of pressure, would be instrumentally more feasible. It was also obvious that any such method as this would have to be carried out on a fairly large scale if temperatures were to be maintained for times sufficient to allow the transition to run appreciably. My previous experiments up to pressures of 50,000 kg/cm² had been carried out in vessels

[1] F. D. Rossini and R. S. Jessup, J. Research Nat. Bur. Stand. 21, 491–513 (1938).
[2] P. W. Bridgman, J. App. Phys. 12, 461–469 (1941).

of only 0.25-inch internal diameter. Rough calculations indicated that in order to maintain temperatures in the reactive region for times of the order of several seconds, which was long enough to seem worth while, an increase would be necessary in the linear dimensions of eightfold, or a 500-fold increase in mass. Apparatus of this magnitude was beyond my own unaided resources, and I was fortunate to obtain the sponsorship and financial support of three commercial companies, which considered the extension of range of conditions beyond those previously utilized in attacking this problem to be sufficient to justify their support. Dr. Zay Jeffries was primarily responsible for making the contacts; the companies were: General Electric, Carborundum, and Norton. Work began under an agreement with these companies in January, 1941. The goal set for the apparatus was 30,000 kg/cm² in a region 2 inches in diameter and several inches long at a temperature above 2000°C, 2500° if possible.

The apparatus was set up and the experiments made in the Dunbar Laboratory of Harvard University. The actual experimental manipulations were conducted by various members of the Norton Company, who were responsible for many of the details of the construction. Especially to be mentioned are: Dr. R. R. Ridgway, Associate Director of Research, Mr. E. J. van der Pyl, during the stages of construction and the early experiments, and in the later stages Dr. S. S. Kistler and Mr. W. M. Wheildon. Mr. L. P. Jensen skillfully performed much of the difficult machine work.

THE APPARATUS AND METHOD

Pressure was produced by a 1000-ton press, of a regular commercial model manufactured by the Watson Stillman Company, with a few minor changes to adapt it to the particular requirements. The ram of the press was 20 inches in diameter, and was actuated by oil, the pressure in which could be raised to 6400 p.s.i. to develop the maximum thrust. The oil pressure was developed by a commercial hydraulic intensifier with 30 to 1 ratio of areas. The large piston of the intensifier was driven by air pressure, stored in a large tank capable of supporting 250 p.s.i. The air pressure was generated by a 3-hp compressor. In operation, pressure in the intensifier was brought to the predetermined maximum by establishing connection with the air reservoir, and then by suddenly opening a valve to the 20-inch ram, pressure was rapidly generated by the action of the ram on the piston, 2 or 1.5 inches in diameter, of the high pressure chamber. The major part of the stroke, before contact was made with the contents of the high pressure vessel, was produced by an auxiliary piston, mounted within and concentrically with the 20-inch ram, so that a stroke of only a few inches was necessary with the 20-inch ram, thus speeding up the action.

The high pressure container was made conical in shape, and the general method of construction was similar to that used in my first experiments to 50,000 kg/cm². In this apparatus external support is given automatically as pressure increases by the thrust on the piston, which drives the whole vessel into external conical supporting rings. The internal diameter of the pressure vessel was 2 inches and the mean external diameter 8 inches. The external supporting block was 10 inches thick and 36 inches external diameter; this was made compound of five disks each 2 inches thick, instead of a single piece, for facility in heat treatment. In the first experiments the whole two inches internal diameter was used, the high pressure piston being 2 inches in diameter; in the later experiments this was reduced to 1.5 inches, combined with various tapered removable liners, to facilitate disassembly and to minimize effects of fracture. In the course of the work several of the containing vessels fractured and several of the supporting disks. The fractures are to be ascribed in part to the fact that it was not possible under wartime conditions to get the desired grades of steel, but there is doubtless in addition a scale effect, making it more difficult with the larger apparatus to reach the 50,000 that had been attained with the original smaller apparatus. The pistons were a source of major difficulty. At first these were of Carboloy; only once was the full 30,000 attained with a Carboloy piston and this fractured after a brief interval. Small test pistons cut from the material of the larger pistons supported more than 50,000, thus indicating a true scale effect. The problem was finally solved by the use of

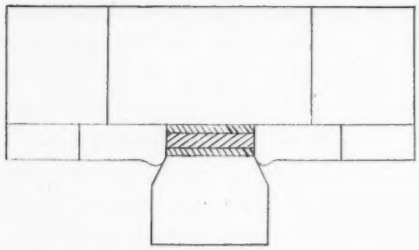

FIG. 1. Method of applying 45,000 atmospheres to hot graphite disk between refractory disks.

steel pistons, which Mr. Whieldon found how to make of the Ajax steel of the Cyclops Steel Company, giving them the special heat treatment, including low temperature soaking, recommended by the manufacturers.

Two types of experiment were performed. In the first a block of graphite was heated to the desired temperature, transferred as rapidly as possible to the pressure chamber and pressure applied. The heating was electrical, by the resistance of the specimen itself. Two graphite electrodes were pressed against the specimen, and current from a transformer capable of delivering 75 kw at 7.5 v stepped down from 2300 v was passed through the specimen until the desired temperature, as indicated on an optical pyrometer, was reached. The graphite block was 1.5 inches in diameter and 2 inches long. When the desired temperature was reached, which might take something of the order of 1 minute, the heating current was broken, the electrodes swung away from the specimen, the specimen pushed home in the pressure chamber by the auxiliary piston, and pressure applied. This sequence of operations was all automatically controlled and consumed altogether about 7 seconds, which was considerably longer than was called for in the original specifications. This time could have been shortened but did not seem worth while in view of the present substitution of the second type of experiment. At first, during the first type of experiment, the 1.5-inch graphite block was pushed by a 2-inch piston into a refractory liner with 0.25-inch thick walls. The expectation was that the refractory, which under normal conditions had little mechanical strength, would crush under the piston, allowing the transfer of full load to the graphite. It developed, however, that under pressures of these magnitudes the refractory assumes so much compressive strength that pressure on the graphite by no means reached the desired value. For this reason the design was later modified, using a 1.5-inch piston, acting directly on the graphite, the refractory liner now being appropriately mounted inside the removable tapered steel liner already mentioned.

In the second type of experiment external electrical heating was replaced by internal heating, produced by a reaction of the thermite type. At first the thermite reaction was used merely to supplement the external heating, in order to compensate for loss of temperature during the unexpectedly long time of transfer to the pressure vessel. This was done by pushing the heated graphite into contact with a thermite charge previously placed inside the pressure vessel. Under these conditions the thermite nearly always failed to ignite, indicating that the surface temperature of the graphite had fallen to less than 1300°C at the moment of contact. In the modified arrangement, the major part of the pressure vessel, inside a refractory liner of graphite, was filled with a modified thermite mixture, capable of giving a higher temperature than the conventional thermite. Embedded in the center was a piece of graphite containing in the later experiments seeds of diamond. Pressure was applied to the cold set-up by suddenly opening the valve to the ram. The mixture contained an igniting arrangement such that when pressure reached a predetermined value, usually between 10,000 and 15,000 kg/cm², the mixture was ignited. The balance of the stroke necessary to bring pressure up to maximum was short, and since the piston was already in motion, required only a small fraction of a second. The reaction was non-explosive in character. One could thus be sure that maximum pressure and temperature were present in the apparatus simultaneously. Pressure was maintained at its maximum while the contents cooled by conduction.

THE EXPERIMENTS AND RESULTS

The experiments with external heating encountered many instrumental difficulties. The preliminary heating of the graphite was usually to 2800°C. Finally a run was made in which it seemed reasonably certain that 30,000 kg/cm² had been applied to graphite at temperatures

well above 2000°C and probably nearer 2500°C. Analysis by the Chemical Laboratory of the Norton Company showed no evidence of any transformation to diamond. The initial material of these experiments was highly purified graphite made in the electric furnace by the Norton Company and had an initial density around 1.9. After exposure to these high temperatures and pressures the theoretical density of 2.25 was permanently acquired. At lower temperatures, however, it proved surprisingly difficult to permanently increase the density by pressure alone, and at room temperature the volume elasticity of commercial graphite of 1.9 density is almost perfect. This may result in very large piston displacements on applying pressure, which on more than one occasion led to the erroneous anticipation that the transition had been effected.

One modified experiment with external heating was made. In this, pressure was pushed to the neighborhood of 45,000 kg/cm², but at the expense of an unknown decrease in the effective temperature. In order to attain this high pressure, advantage was taken of a phenomenon which I had previously utilized[3] in my experiments combining high pressure with shearing stress. It is possible, in small localized regions, to reach much higher stresses than can be attained in homogeneously stressed regions because of the support afforded by the surrounding unstressed parts. The experimental arrangements are indicated in Fig. 1. The plane face, 1.5 inches in diameter, of a truncated Carboloy cone, compresses a disk of graphite 0.25 inch thick against the plane face of a massive steel block hardened to maximum hardness. In order to minimize lateral escape of the graphite, the disk is surrounded by a retaining ring of alloy steel in which the Carboloy cone embeds itself. The retaining ring was heat treated to hardness about 40 on the Rockwell *C* scale. The graphite disk was heated to a preliminary 2800°C electrically as in the other method, and then swept by the onrushing piston into forcible contact with the massive block. Direct contact between metal parts and the hot graphite was prevented by refractory disks. Because of the small travel distances, the time interval between cessation of heating and the maximum pressure was notably less than in the previous method, but on the other hand, because of the smaller mass of graphite, cooling was more rapid. The result of the experiment was negative. There was copious and dramatic evidence of the magnitude of the stress in the manner in which the graphite was extruded laterally into the retaining steel ring, and there was also evidence of the high temperatures on the surfaces surrounding the graphite in the way in which cracks in the hardened steel had been melted together again. It would be hazardous to estimate the maximum temperature in the interior of the graphite, and the times, and I shall not attempt it. One of the factors to be considered in any calculation is that the mechanical energy of the lateral extrusion was sufficient to raise the temperature 500°C.

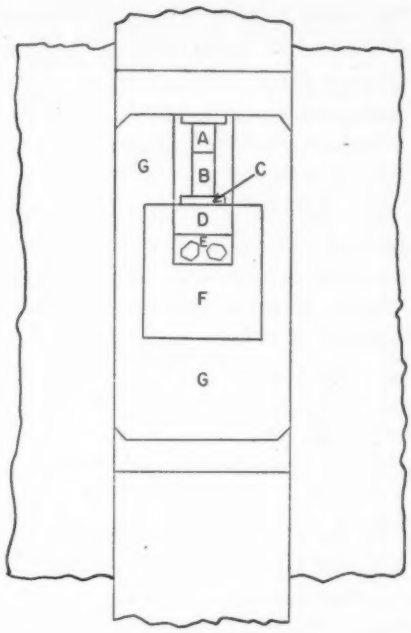

FIG. 2. Apparatus for combining internal heating with pressure. A, tetracene; B, empty space; C, shear plate of hardened steel; D, "igniter" charge; E, diamond seed crystals embedded in powdered graphite; F, main charge for exothermic reaction; G, massive graphite. The other parts are of steel.

The second type of experiment, with internal heating, involved much preliminary work, both to get the proper geometrical arrangements so that ignition of the charge would reliably occur, and also to find the proper chemical compositions for the charge to develop the required amount of

[3] P. W. Bridgman, Phys. Rev. **48**, 825–847 (1935).

heat. The conventional thermite mixture was entirely unsuitable, being difficult to ignite, and not developing enough heat. The general arrangement finally adopted is shown in Fig. 2. The reaction is initiated by impact of a fractured shear plate against a pellet of "tetracene." This sets off the "igniter" charge, which in a typical case consisted of 0.080 g sugar and $KClO_3$ mixture plus 0.360 g Mg and Na_2O_2 mixture. The igniter charge in turn sets off the main charge. The composition of the main charge, which in the final experiments weighed 25 g, varied according to the temperature to be reached. The mixture giving the highest temperature was compounded out of 25 percent of a mixture of Mg and Na_2O_2 and 75 percent of a mixture of Mg and $KClO_3$, the latter containing 30 percent excess Mg. For the lowest temperature 13 grams of the mixture just specified was mixed with 12 grams MgO. The temperatures to be expected were calculated by W. F. Moy of the Research Staff of Norton Company and varied from 6350°K for the first to 3000°K. The calculation was on the basis of 100 percent efficiency, all the heat being assumed retained in the reacting mass. It would have been difficult to apply all the corrections involved in making a satisfactory calculation of the difference between the theoretical maximum temperature and that actually reached. The time of the reaction is an element of uncertainty; it was not explosive and there was no external indication when the piston was pushed home as to whether the reaction had run or not. The actual temperature was, therefore, roughly obtained by using a small disk of molybdenum embedded in the mixture. This was always found to have been fused with mixtures giving a theoretical maximum temperature of 3660°K or higher. Allowing an increase of the melting point of molybdenum of 100° above normal for the effect of pressure, this would indicate a loss from the theoretically calculated maximum temperature of not more than 700°.

The experiments with internal heating differed from those with external heating in that diamond seed crystals were used. Three of these were usually used in each experiment, weighing approximately 0.1 g apiece. They were embedded in a graphite capsule weighing about 0.6 g. The degree of graphitization produced was determined by the Chemistry Section of the Norton Company under the direction of Dr. N. W. Thibault, by treatment with perchloric acid and weighing the unaltered residue.

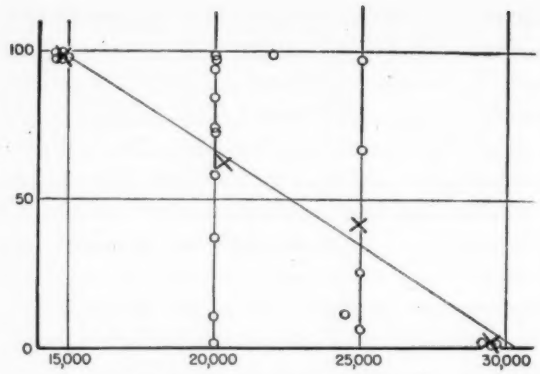

FIG. 3. Percentage of graphitization plotted as ordinate against pressure in kg/cm² as abscissa. The crosses show the group averages and the circles the individual readings.

The first experiments were made at a constant pressure of 20,000 kg/cm² with a variety of temperatures. In these experiments total graphitization was found at the higher temperatures and none at all at the lower temperatures. X-ray analysis showed that the graphitized diamond had the same crystal structure as normal graphite. This establishes the fact that the problem is not complicated by the existence of previously unknown intermediate modifications between diamond and graphite. An experiment at 30,000 kg/cm² at a temperature where there was no graphitization also established the absence of any transition in the reverse direction from graphite to diamond.

In spite of this negative result, indicating that the transition would not run under the conditions attainable with the apparatus, it appeared that positive indications might possibly be attained as to the location of the transition pressure in this temperature range. If this could be done, the whole diamond problem would obviously be much nearer solution. After some trial, for the experimental conditions were somewhat sensitive, a proper mixture, that is, a temperature, was found such that at this temperature graphitization was only partial. Now keeping the mixture and, therefore, presumably the temperature constant the percentage of graphitization was determined as a function of pressure in the range from 15,000 to 30,000 kg/cm². The results

are shown in Fig. 3. The five runs at 15,000 all gave practically 100 (99.9) percent graphitization, and the three at 30,000 all practically 0 percent (0.2, 1.0, and 0.3 percent). The intermediate runs at 20,000 (11 points), and 25,000 (5 points) show a wide degree of scattering, but the trend is unmistakable, and, as a matter of fact, the averages at 20,000 and 25,000 lie not far out of line with the points at 15,000 and 30,000.

A literal interpretation of these results would, therefore, indicate by extrapolation that above 30,000 kg/cm² at this temperature, that is, slightly above the melting point of molybdenum, the percentage of graphitization will be negative, or in other words that the transition from graphite to diamond will actually go under these conditions. The true significance of these results is obscured by the scattering of the points, the complexity of the experimental conditions, and the possibility of a region of indifference between graphite and diamond. It would seem that these experiments have at least established an effect of pressure on the transition, of which there was no previous direct evidence. Further experiments are obviously called for, but at this stage of the investigation the time limit on the contractual relations with the three companies expired, and there is no present prospect that I will be able to continue the investigation.

APPENDIX

Two points require comment in this appendix.

In the first place there is considerable superficial resemblance between the first experiments with external heating and experiments, also negative, by Günther, Geselle, and Rebentisch,[4] published in 1943. These experimenters also heated graphite externally, which was then swept by a rapidly moving piston into the pressure vessel. The initial temperature was between 3000 and 3200°C. The graphite specimen was small, being in the form of a thin disk of unspecified thickness and 8 mm in diameter. All parts of the apparatus were of steel. No method of automatic external support of the steel was employed, but merely conventional methods of shrunk on members. Momentary pressures as high as 120,000 kg/cm² and static pressures of 100,000 kg/cm² were claimed. Stresses of these magnitudes in steel under these conditions may, I believe, be absolutely ruled out, so that it is probable that the pressures and temperatures actually reached were materially less than those claimed. Friction and binding of the steel pistons (not corrected for) would account for too high stresses, and the small size of the specimen for too high temperatures.

The second point concerns the calculation from thermodynamic data of the relation between pressure and temperature for the reversible transition. The fundamental data, which by universal consent seem to have been accepted as best, are summarized in a paper by Rossini and Jessup in 1938,[1] supplemented by slightly improved data in the paper by Prosen, Jessup, and Rossini[5] of 1944. In the 1938 paper Rossini and Jessup also discussed the most probable relation between pressure and temperature for the reversible transition, and this discussion has been accepted by other authors as the basis for various estimates as to the transition parameters. All these estimates agree in predicting, for temperatures of 2000° or more, pressures considerably higher than 30,000. For example, Leipunskii[6] estimates 60,000 kg/cm² at 2000°C and Goranson[7] 50,000 kg/cm² at 1000°C. Some comment seems, therefore, called for on the degree of probability that can be attached to an extrapolation of Rossini and Jessup's equation.

The great improvement effected by Rossini and Jessup over previous work was in a better value for the heat of combustion. Recent methods of manufacture have produced a graphite pure enough to give reproducible and reliable values for the heat of combustion, so that in determining the energy content of carbon compounds it is now possible to dispense with the expensive procedure of burning diamonds, which had previously been necessary because of the inferior quality of the available graphite. The difference of the heats of combustion between diamond and graphite enters into the free energy of transition from diamond to graphite, so that a much improved value for this was possible, which was calculated by Rossini and Jessup. But it is important to notice that the improvement affects only the constant term in the free energy. The terms involving the variation of free energy with pressure and temperature are in no wise affected by the work of Rossini and Jessup and continue to rest on the old measurements with unsatisfactory grades of graphite.

The relations of the various factors may be exhibited by writing the equation for the difference of free energy in the form:

$$\Delta F(p_1\tau) = \Delta H_0 - \tau\Delta S_0 + \left\{\int_{\tau_0}^{\tau}\Delta C_p d\tau - \tau\int_{\tau_0}^{\tau}\frac{\Delta C_p}{\tau}d\tau\right\} + \int_{p_0}^{p}\Delta v dp.$$

Here F is the Gibbs thermodynamic potential, defined as $F=E-\tau S+pv$, where the letters have their customary significance. ΔF is defined as $\Delta F \equiv F(\text{diamond}) - F(\text{graphite})$. ΔH_0 is by definition the difference of total heats at an arbitrary temperature τ_0 at atmospheric pressure $\{\Delta H_0 = H_{\tau_0}(\text{diamond}) - H_{\tau_0}(\text{graphite})\}$ and may be obtained experimentally from the difference of heats of combustion. ΔS_0 is by definition the difference of entropies at τ_0 and atmospheric pressure. $\{\Delta S_0 = S_{\tau_0}(\text{diamond})$

[4] P. L. Günther, P. Geselle, and W. Rebentisch, Zeits. f. anorg. allgen. Chem. **250**, 357 (1943).

[5] E. J. Prosen, R. S. Jessup, and F. D. Rossini, J. Research Nat. Bur. Stand. **33**, 447–449 (1944).

[6] O. I. Leipunskii, Uspekhi Khimii **8**, 1519–1538 (1939).

[7] R. W. Goranson, Sci. Mon. **51**, 528 (1940).

$-S_{\tau_0}$(graphite)}. ΔC_p is the difference of C_p at atmospheric pressure and is a function of temperature. {$\Delta C_p = C_p$(diamond)$-C_p$(graphite)}. Δv is the difference of volume {$\Delta v = v$(diamond)$-v$(graphite)} and is intrinsically negative. The integration with respect to pressure is performed at temperature τ from atmospheric pressure to p. The transition always runs either with decreasing F or, in the limit at equilibrium, with no change in F. Under ordinary conditions the phase which has the larger F is the unstable phase.

If it can be assumed that at atmospheric pressure ΔC_p becomes and remains zero above a certain temperature, then above this temperature ΔF is approximately linear in pressure and temperature. This is the assumption that has been made by various authors in extrapolating to higher temperatures. The data have been directly determined only to 1100°C and Rossini and Jessup have been careful in their paper to state that this is the range of applicability of their formulas. What now is the probability of a vanishing of ΔC_p above a certain temperature and an eventual linear course of the curve? From the theoretical point of view, as suggested by Dulong and Petit's law, and neglecting electronic contributions, it would be expected that eventually C_v rather than C_p would become equal at high temperatures. But now C_p and C_v for diamond and graphite differ by an abnormally large amount. The relation is given by the formula

$$C_p = C_v - \tau\left(\frac{\partial v}{\partial \tau}\right)_p^2 \Big/ \left(\frac{\partial v}{\partial p}\right)_\tau.$$

The difference between C_p and C_v, particularly at the higher temperatures, is abnormally large for diamond both because its compressibility is abnormally small, being 30 times less than that of graphite, and because its thermal expansion appears to rise abnormally rapidly. The formulas for best volumes quoted by Rossini and Jessup indicate that at 1000°K the thermal expansion of diamond is 36 percent greater than that of graphite. Altogether, the excess of C_p over C_v is 60 times greater for diamond than graphite at 1000°K and increases further with rise of temperature. At this temperature C_p for diamond is 15 percent greater than C_v. Furthermore, the best formula quoted by Rossini and Jessup for specific heats gives a *reversal* of sign for the difference of C_p at 1100°C.

Altogether it is, therefore, probable that above 1000°K the contribution of the terms $\int_{\tau_0}^{\tau} \Delta C_p d\tau - \tau \int_{\tau_0}^{\tau} \frac{\Delta C_p}{\tau} d\tau$ to the thermodynamic potential tends to become increasingly negative. This means that the transition curve is not linear, but the slope, $d\tau/dP$, rises increasingly, and the pressure obtained by linear extrapolation becomes increasingly too high.

Another much rougher and more elementary argument indicates the plausibility of an upward curvature of the equilibrium line. The slope of the transition line is, according to Clapeyron's equation:

$$d\tau/dp = \tau \Delta v/L.$$

Any variations in Δv may be expected to be of relatively minor importance because of the abnormally large absolute value of Δv for this transition, with the result that any effects of pressure and temperature on Δv would be expected to be of less importance than for more normal substances. Also the variation in latent heat may be expected to be relatively small in view of the direct experimental results which I have found for a large number of polymorphic transitions measured under pressure. This leaves outstanding, therefore, that $d\tau/dp$ is approximately proportional to the absolute temperature, and therefore the equilibrium line curves upward.

All things considered, it would seem to me that there are possibilities of such large uncertainties in the calculation of the thermodynamic parameters of the transition line in the extrapolated temperature region, between 2000° and 3000°C, that little more than an indication as to orders of magnitude can be expected. Greater weight should, I believe, be attached to the location of the curve suggested by the experimental determination of the change with pressure of the inversion velocity as described in this paper.

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Motions of Molecules in Condensed Systems III. The Infra-Red Spectra for Cyclohexane Solid II, Solid I, Liquid and Vapor in the Range from 3 to 15μ*

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Infra-red spectra are compared throughout the interval from 650 to 3300 wave numbers for the same amount of cyclohexane when it exists separately as vapor at 20°, liquid at 10°, and solid I at 3°C, likewise in the intervals from 700 to 1600 and 2500 to 3300 wave numbers when it exists as solid I at −75° and solid II at −100°C. The four spectra obtained with the condensed phases are quite similar and differ only slightly from the one for the vapor. These results contrast sharply with ones reported previously for a similar study of benzene and indicate that there is a greater semblance of order in liquid cyclohexane than in liquid benzene. The spectra are consistent with, but yield no constructive evidence to confirm or deny the notion that molecules of cyclohexane are able to rotate freely in solid I. Developments attributable to intermolecular forces, although not spectacular, contain new information about the numbers and positions of bands which may prove useful toward assigning frequencies to normal modes of vibration in the isolated molecule of cyclohexane. The results of this study do not contradict any of the principles set forth in the first paper of this series.

INTRODUCTION

MUCH information pertaining to condensed phases might be obtained from the infra-red absorption spectra of liquids and solids if the theoretical treatment were as complete as that for the spectra of vapors. The first paper[1] of this series described some useful simplifications of the theoretical problem whereby the spectrum of a molecular crystal is interpreted in terms of the motions of an isolated molecule. This approach makes possible the prediction of approximate selection rules for such crystals and indicates also that there are no selection rules operating in the liquid state.

This treatment was tested by application to benzene, reported in the second paper,[2] and was found capable of explaining all the important new features of the spectra of liquid and solid.

The present paper compares the infra-red absorption spectra of cyclohexane in the vapor, liquid, and two solid forms over the range from 650 to 3300 wave numbers. The results are examined in the light of the principles set forth in I. The infra-red spectra of the two solid forms have not been reported previously, although the vapor and liquid have been examined by other workers.[3a, b] It was, however, necessary to re-examine these states in order to avoid comparison difficulties arising from different resolutions, sample thicknesses, etc., in the various published results.

Cyclohexane was chosen for examination because of its convenient physical characteristics, being easily produced in vapor, liquid, and two solid states; the higher temperature solid is of interest in that probably its molecules rotate in the crystal lattice. In addition, the substance is well suited for comparison with results reported previously for benzene.

EXPERIMENTAL

The cyclohexane was Standard Sample 209 obtained from the National Bureau of Standards, Washington, D. C. Although no assay was furnished with the individual sample, a prospectus advertised it to be 99.98±.02 percent pure. After opening, the original ampule was stored in a

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[1] R. S. Halford, J. Chem. Phys. 14, 8 (1946), hereafter referred to as I.

[2] R. S. Halford and O. A. Schaeffer, J. Chem. Phys. 14, 141 (1946), hereafter referred to as II.

[3] a. C. F. Kettering and W. W. Sleator, Physics 4, 39 (1933); P. Lambert and J. Lecomte, Ann. de physique 18, 329 (1932); R. S. Rasmussen, J. Chem. Phys. 11, 249 (1943); b. A. P. I. Research Project No. 44: Spectrograms 16 and 17, contributed by Shell Development Company, Emeryville, California, and Spectrogram 116, contributed by University of Oklahoma Research Institute, Norman, Oklahoma. All spectrograms available at National Bureau of Standards, Washington, D. C.

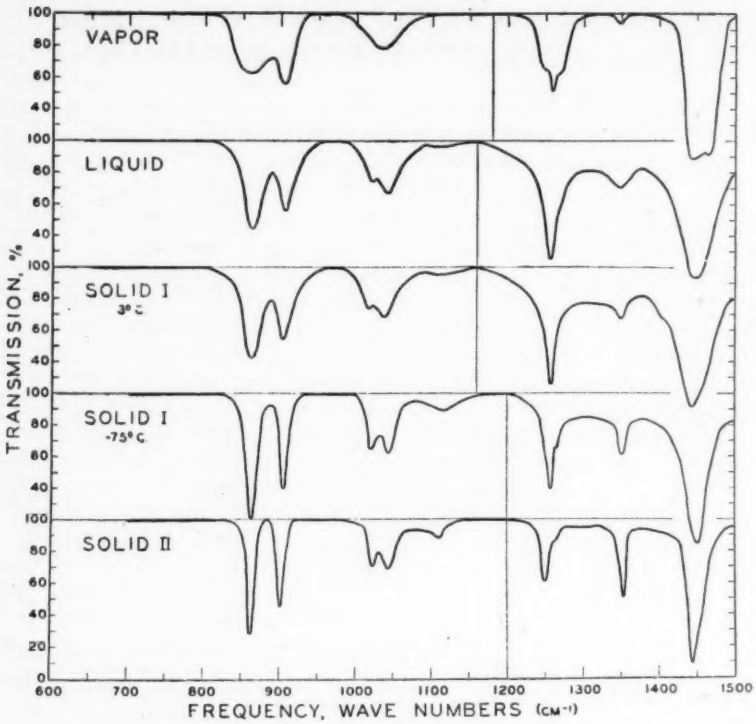

FIG. 1. Infra-red absorption spectra for equivalent absorbing paths of cyclohexane vapor (42 mm in a 30-cm cell at 25°C), liquid (0.065 mm thickness at 10°C), solid I (same specimen at 3°C), solid I (same specimen at −75°C), solid II (same specimen at −100°C). Observations below 1150–1200 cm^{-1} with rocksalt prism, others with fluorite prism. Results for lowest two temperatures not strictly comparable to others.

small outer container in an atmosphere of dry air, and the contents were used without further treatment.

The absorption cell for the vapor specimen was of conventional design, a glass tube 30 centimeters long sealed at both ends with rocksalt windows. An otherwise identical, evacuated cell was employed for the photometric standard ("blank" cell).

The rocksalt (or potassium bromide) absorption cells for the condensed samples at 10° and 3°C were made, filled, supported, and thermostated as described in II. Glycerin, used to seal the edges of these cells, is not appreciably soluble in cyclohexane. As in II, a single piece of polished rocksalt (or potassium bromide) was used as the blank, since the reflection at the two air-salt interfaces is the chief variable for which the blank must compensate.

The absorption cell thermostat for the solid samples at −75° and −100°C was that described by Halford and Karplus,[4] with the following modification. The arrangement of cooling coils around the sample and the connected flexible metal tubing was retained, but the system for pumping a cooling liquid through the coils was not used because of the lack of such a liquid which would flow also through coils in a bath of liquid nitrogen—the most convenient cooling agent. Instead, the liquid nitrogen was poured intermittently into a funnel sealed to one end of the flexible tubing leading to the coils around the cell; a stopper was placed loosely into the top of the funnel so that the pressure developed by the evaporated nitrogen forced the remaining liquid through to the coils. The liquid nitrogen was added necessarily in small increments and the frequency of addition determined the temperature obtained. The heat capacity of the coils was sufficiently large that no great changes of temperature could occur in the sample in this procedure. The rocksalt (or potassium bromide) cell for the sample was the same as in runs made at higher temperatures.

All observations were made with an automatic recording prism spectrophotometer;[5] for the privilege of using this apparatus, we are indebted to Professor Wilson.

The vapor sample was observed at room temperature. Each liquid specimen was cooled to

[4] R. S. Halford and R. Karplus, in preparation.

[5] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. 6, 197 (1938).

about 10°C and maintained at that temperature while its spectrum was recorded. It was then frozen (6.6°C) and subsequently held at about 3°C while the corresponding spectrum of the solid was recorded. Solidification of the cyclohexane specimen in the cell occurred abruptly but without drastic supercooling, in contrast to the earlier experience with benzene (II). The resulting solid was almost perfectly transparent; only the presence of faint, seemingly parallel striations, which formed on cooling and disappeared on rewarming through the melting point, revealed its crystalline nature. A slight but easily detectable decrease of transmission was observed with the spectrophotometer as an accompaniment to solidification and served to confirm the change. The transmission of the solid did not increase appreciably on standing, as did that of solid benzene, but was quite high from the instant of freezing. This solid (hereafter called solid I) is stable between the freezing point and −87.0°C, at which point transition[6] to a different crystal structure takes place. The spectrum of solid I was observed also at −75°C. The same sample was then cooled to −100°C and held there as the spectrum was recorded. The occurrence of the change in crystal structure was evidenced by an abrupt drop in the transmission of the sample as it was cooled; this is presumably due to the formation of numerous small cracks resulting from the contraction in volume at the transition.

In the interval between the observations at higher and lower temperatures, modifications were made in the spectrophotometer which resulted in a substantial increase of resolving power. For this reason the two sets of spectra are not strictly comparable.

RESULTS

Figures 1 and 2 show the relative transmissions as a function of frequency in wave numbers, in the range from 650 to 3300 wave numbers, for the same amount of cyclohexane when it exists separately as vapor, liquid, solid I at 3° and −75°C, and solid II. The high temperature form, solid I, was examined near both ends of its range of stability in order to facilitate comparison with adjacent states. The entire range of frequencies was examined with liquid and solid samples approximately 65 microns thick, and with a vapor

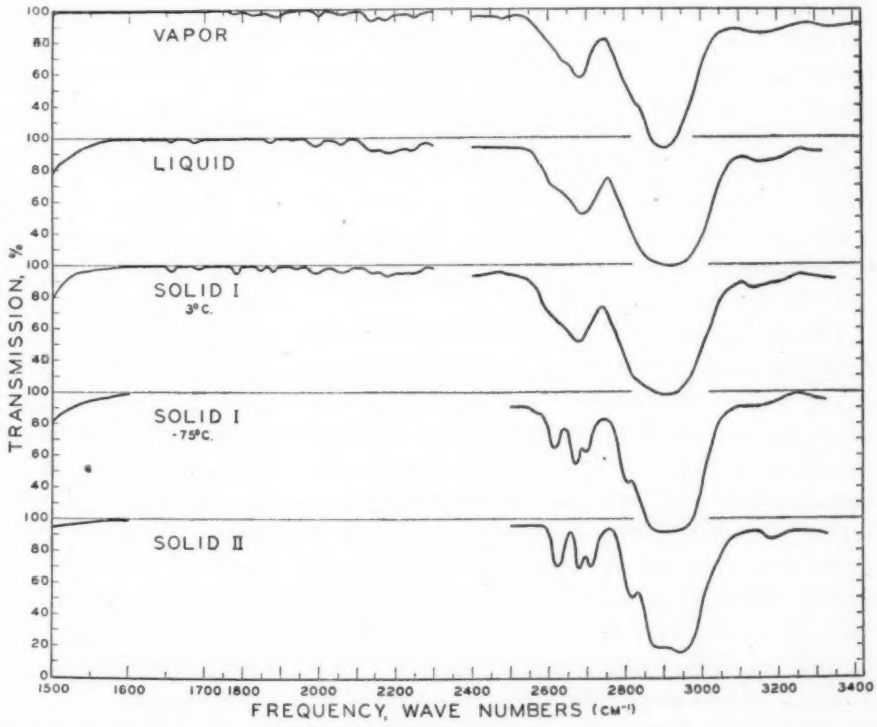

FIG. 2. Infra-red absorption spectra for equivalent absorbing paths of cyclohexane vapor (42 mm in a 30-cm cell at 25°C), liquid (0.065 mm thickness at 10°C), solid I (same specimen at 3°C), solid I (same specimen at −75°C), solid II (same specimen at −100°C). All observations with fluorite prism. Results for lowest two temperatures not strictly comparable to others.

[6] J. G. Aston, G. J. Szasz, and H. L. Fink, J. Am. Chem. Soc. **65**, 1135 (1943); R. A. Ruehrwein and H. M. Huffman, J. Am. Chem. Soc. **65**, 1620 (1943).

TABLE I. The locations and absorptions of the centers of prominent bands in the infra-red spectra of cyclohexane in different states.

Vapor		Liquid		Solid I (3°)		Solid I (−75°)		Solid II	
$\tilde{\nu}$ (cm^{-1})	A(%)	$\tilde{\nu}$ (cm^{-1})	A(%)	$\tilde{\nu}$ (cm^{-1})	A(%)	$\tilde{\nu}$ (cm^{-1})	A(%)	$\tilde{\nu}$ (cm^{-1})	A(%)
527*	(8)*								
862	37	862	55	862	57	861	79	862	71
905	44	904	44	903	46	905	59	901	55
		1021	25	1019	26	1020	35	1024	30
1037	21	1041	33	1038	31	1043	37	1045	31
		1112	(3)	1112	(4)	1113	(10)	1113	(11)
1260	48	1258	73	1258	73	1258	60	1251	38
						1266	(10)	1265	(8)
1348	(5)	1352	(30)	1351	(33)	1353	38	1354	49
1457	92	1449	87	1447	88	1451	95	1444	91
2630*s*	(10)	2610*s*	(10)	2610*s*	(10)	2620	(35)	2624	29
2685	43	2695	48	2680	48	2670	(45)	2680	30
						2695	(30)	2710	(18)
2810*s*	(5)	?		?		2810*s*	(12)	2820	(25)
2905	87	2915	81	2910	82	2920	88	2920	84
3135	(10)	3170	(10)	3165	(10)	3160	(8)	3180	(10)

* Observed with 100-mm Hg pressure of vapor.

sample contained in our cell under a pressure of 42 millimeters of mercury, which provides the number of molecules equivalent to a 65-micron thickness of liquid or solid. In addition, samples of condensed states 20 and 170 microns thick were observed less intensively as an aid to interpretation of the spectra. In the interest of clarity, the figures include only the observations made on the intermediate thickness, but with refinements verified by the additional information: the thinnest sample served to verify the resolution shown for the more intense absorptions, while the thickest one confirmed the reality of the weaker components. For all condensed states, wherever there was any doubt as to the result, or where the spectrum seemed to be of special significance, observations were repeated as required to establish the results.

The low temperature results are somewhat less extensive than those for higher temperatures because of the difficulty in carrying out these observations. The data extend down to 700 wave numbers, and the relatively unimportant region between 1600 and 2500 wave numbers is not reported since our data here are sufficient only to show that there are no large changes from the results obtained at higher temperatures. In all spectra, no accurate data were obtained in the vicinity of 2350 wave numbers because of the presence of the extremely strong absorption by the carbon dioxide in the atmosphere. This cuts down the incident light intensity to values too low for accurate work; we may, however, report that there are no intense bands in this region.

The curves for the lowest two temperatures are not completely comparable with those at higher temperatures because the resolving power of the spectrophotometer was increased between the determination of the latter and the former. Part of the obvious sharpening of bands in the low temperature spectra then is caused by increased resolution, and the remaining sharpening is to be attributed to the temperature effect.

In Table I are listed the positions of the band centers for the more important bands of cyclohexane, together with the corresponding measures of absorption, which are the depths of the band centers measured in percent of light transmitted. Table II gives the same information, where it is available, for the weaker bands which appear in regions where no fundamentals are expected. The absorption values in Table II are for a 170-micron sample, in order that the relative values be significant. The measurement of position of a band center is reproducible to within a few tenths of one percent of the value quoted for its frequency. We believe that the accuracy is about the same. The measures of absorption have been corrected for losses by reflection but not for stray light passing through the spectrophotometer. The former corrections were small but variable from state to state. The latter ones may amount to as much as ten percent of the incident radiation in the worst case, are variable from place to place

on the frequency scale, but enter all three spectra similarly, and hence do not affect a comparison at the same frequency of the relative intensities of absorption by cyclohexane in the four states. Less reliable measurements are enclosed in parentheses.

Table I also includes a very weak band at 527 wave numbers which was observed with a vapor sample in our cell under a pressure of 100 millimeters of mercury. It is certainly too weak to detect in a cell containing much less cyclohexane. Data have not yet been obtained in this region for the other states.

The spectra observed by us for the vapor and liquid are for the most part in excellent agreement with those reported by others.[3] We believe that ours is the only comprehensive study of the spectra for the solid forms of cyclohexane.

The most notable discrepancy between our observations and prior ones occurs in the region just below 700 wave numbers. Whereas we find this region to be transparent for vapor, liquid, and solid I, Lambert and Lecomte[3] report absorption by the liquid at 678; Kettering and Sleator,[3] by the vapor at about 670; Rasmussen,[3] by the vapor at 673 wave numbers; the other investigators cited did not examine this region. In our first observation with the vapor, we encountered a weak band with *P*-, *Q*-, and *R*-branches, centered at about 670 wave numbers. However, when careful attention was given to sources of contamination in the cell and accessories for filling it, this band disappeared. It never appeared in the other states. We have reason to believe that, in our case, the spurious absorption was caused by a well-known and extremely intense component of the spectrum for benzene. It seems likely that this contaminant might have been present in the specimens examined by those other workers‡ who found a band in the same vicinity. We have not yet sought this absorption in solid II, but it is difficult to see how it could appear there if it does not also appear in the liquid.

We attach no significance to the indentation shown on the bottom of the intense band at 1457 in the spectrum of the vapor as our observations with this part of the vapor spectrum were not sufficient to establish its reality.

The region between 1500 and 2500 wave numbers shows numerous weak absorptions. We have confirmed those shown for the liquid and solid I by noting that they intensify with increasing sample thickness. Although the absorption of the atmospheric water vapor in the light path complicates measurements throughout a large part of this region by causing sharp fluctuations in the intensity of the incident light, the blank compensates for this difficulty. Our results concerning the spectrum for the liquid here agree with independent observations[7] made by means of a spectrophotometer with an evacuated light path and consequent freedom from atmospheric complications. Our data alone do not prove beyond doubt the existence of the corresponding bands in the vapor spectrum, but the necessary confirmation can be found in other observations. We conclude that most, if not all, of these numerous weak absorptions are actually present in vapor, liquid, and solid I, although the shapes of the band envelopes are often somewhat altered by the changes of state.

DISCUSSION

The spectra observed with all four phases are interpretable, according to the principles developed in I, in terms of the motions of an isolated molecule. A cyclohexane molecule has forty-eight fundamental internal modes of vibration. Some of these are expected to have frequencies below

TABLE II. The locations and absorptions of the centers of the less prominent bands in the infra-red spectra of cyclohexane liquid and solid I (170 micron sample).

Liquid		Solid I (3°C)	
$\tilde{\nu}$ (cm^{-1})	A(%)	$\tilde{\nu}$ (cm^{-1})	A(%)
1648	8	1649	8
1685	12	1685	13
1695*s*	(5)	1695*s*	(6)
1780	11	1780	13
1832	5	1832	7
1874	12	1875	14
1932	3	1934	4
1989	16	1990	17
2059	11	2062	14
2136	21	2139	22
2182	23	2183	24
2214*s*	(8)	2218*s*	(8)
2247	23	2249	25
2494*s*	(11)	2495*s*	(12)

‡ E. K. Plyler, in a private communication to F. G. Brickwedde, M. Moskow, and J. G. Aston, J. Research Nat. Bur. Stand. **37**, 263 (1946), states that there is no band at 673 in the spectrum of pure cyclohexane.

[7] Spectrogram 16, reference 3b.

the range of our observations, but their number is small. Therefore, the comparative scarcity of components in the infra-red spectrum of the vapor is presumptive evidence that rather strict selection rules are operating in the isolated molecule. This assertion is supported by the appearance of the Raman spectrum. The totality of evidence[8] along these lines, including depolarization factors and Raman effect, weighs heavily in favor of the "chair" structure, with symmetry D_{3d}. This form differs from the "boat" structure mainly in that rotation to the "opposed" configuration has taken place about two of the six carbon-carbon single bonds. From an order-of-magnitude estimate of 3000 calories per mole for the height of the potential barrier restricting rotation about such a bond, and from the assumption that the "staggered" configuration represents the minimum potential energy, one can use the Boltzmann distribution to estimate that the portion of molecules in the boat form is perhaps of the order of 0.01 percent: utterly negligible for our considerations.

Comparison of Vapor and Liquid

It was predicted generally in I, and confirmed for the case of benzene in II, that there are no selection rules operating in the liquid phase, although the intensities of bands which appear only in the liquid spectra are relatively lower than those of bands which appear also in the vapor. One would expect therefore that the infra-red spectrum of cyclohexane should be enriched by a large number of weaker components as a result of its condensation, whereas upon first examination of the spectra, it may appear that such is not the case. There are, however, a number of changes induced by condensation: the doublet structure which develops around 1030, the shallow band at about 1115, the broad shoulder on the low frequency side of the band near 1260, the intensification of the 1350 band, and the pronounced broadening of absorption occurring in the vicinity of 2900 wave numbers. These changes are fairly numerous although they are in no way spectacular. They are probably accompanied by other changes too small to be detected.

These developments attending condensation of cyclohexane, as summarized in the preceding paragraph, are in distinct contrast to those observed with benzene. With the latter substance, a number of components, forbidden in the spectrum of the vapor, achieve some prominence in the spectrum of the liquid. Outstanding are a group of bands, the centers of which correspond to all the principal frequencies in the Raman spectrum of benzene. Now for cyclohexane, the more important contributions to the Raman spectrum are found[9] at 802, 1029, 1158, 1267, 1348, 1445, and between 2854 and 2935 wave numbers, excluding ones that fall outside the range of available infra-red data. At some of these locations, weak developments in the infra-red spectrum of the liquid might be obscured by the more intense absorption carried over from the spectrum of the vapor, but not so at 802 and 1158, and possibly also at 1029 and in the neighborhood of 2900 wave numbers. Indeed, developments are found around 1029, 1348, and 2900 which might, however, originate in modes of vibration other than the ones concerned in the Raman spectrum. At 802 we detected, with a 170 micron sample thickness, a possible faint trace of absorption, so weak (not more than 2 percent) that it remains uncertain; at 1158, similarly, we found no absorption whatever. It is for frequencies in these latter regions that the most spectacular changes take place for benzene.

This dissimilarity between the two substances seems somewhat surprising when one considers that the intensity of developments of the kind in question are dependent on the intermolecular forces for which the gross measures, such as the heat of vaporization and the boiling point, are quite similar for benzene and cyclohexane. One hypothesis will be offered for consideration. The intermolecular potential energy arises from the instantaneous polarization of a molecule by its neighbors, and accordingly is determined in part by the molecular polarizability. To a fair approximation, the latter is an additive property of the various structural features, and is numerically very similar for benzene and cyclohexane. For benzene, however, the principal contribution arises from the electrons in the ring, whereas in

[8] This evidence is summarized by K. W. F. Kohlrausch and W. Stockmair, Zeits. f. physik. Chemie **B31**, 382 (1935), and R. S. Rasmussen, reference 3.

[9] A. Langseth and B. Bak, J. Chem. Phys. **8**, 403 (1940).

cyclohexane, it arises from the electrons shared by hydrogen and carbon. Thus we should expect that the "ring modes" in benzene and the "hydrogen modes" in cyclohexane will be, in each case, the ones more strongly influenced by the perturbing effect of the molecular environment. For both molecules, the ring modes lie mostly below 1350, while the hydrogen modes fall mostly above 1200 wave numbers. The observed developments are most prominent with benzene in the former range, and with cyclohexane in the latter range.

Any such hypothesis which serves only to emphasize one region of the spectrum relative to another seems incapable of accounting completely for the generally lesser intensity of developments throughout the spectrum of cyclohexane, especially at 802 and 1158 wave numbers. For this reason, it appears necessary to suppose that there is more semblance of orderly arrangement in liquid cyclohexane than in liquid benzene. The minimum symmetry of the environment of an arbitrary molecule which provides for mutually exclusive Raman and infra-red spectra possesses a center of inversion; the arrangement of molecules in liquid cyclohexane must approximate this symmetry. Furthermore, since the absorption process is practically instantaneous, relative to nuclear motions, this approximation must apply at any instant rather than merely as a time-average. A similar conclusion is indicated also by the observation that the x-ray diffraction pattern of liquid cyclohexane is somewhat sharper than the one of liquid benzene.[10]

Whatever may be the proper interpretation for the dissimilarity between benzene and cyclohexane, we regard the fact itself, because it seems surprising, as strong encouragement for our belief in the discriminatory powers of the line of investigation we have been following in these studies.

In addition to the Raman-active frequencies, there should appear also in the infra-red spectrum of the liquid frequencies which are prohibited from appearing in either spectrum for the vapor state. There are five such inactive fundamentals, all in the region from 700 to 1350 wave numbers,[11] of which only one has been estimated to more than one significant figure. This is the inactive ring mode which Saksena[12] calculated to be near 1110 wave numbers, on the basis of a very simple model of the cyclohexane molecule. (This absorption could appear in the spectrum of the liquid even if the latter had an actual center of symmetry.) We find that a weak band does appear at 1112 wave numbers in the liquid spectrum. We cannot say, however, that this band might not originate in some other mode or combination of modes.

Comparison of Liquid and Solid I

The striking similarity of the spectra for the liquid and the high temperature form of the solid must be regarded as indicating a corresponding similarity in structure of the two phases. Again this is in marked contrast with the state of affairs in the benzene spectra where some of the bands which appear first in the liquid disappear on freezing due to the increased symmetry in the crystal. But in the case of cyclohexane, once the spectrum of the liquid had been examined, we could expect no result other than the one obtained; no large bands emerge in the liquid, so none of them can disappear on passing to the solid. Beyond this, however, we notice that those small changes which developed in the liquid remain also in solid I.

A facile explanation of the difference in behavior of the two substances is that the molecules of cyclohexane probably rotate in the crystal lattice of the high temperature form (solid I), while those of benzene do not rotate in the solid. This is, however, unsatisfactory, because no abrupt changes occur on passing through the solid I–solid II transition point, where rotation is presumed to stop.

We may conclude that the intermolecular forces in cyclohexane are changed less than those of benzene on passing from liquid to solid, from the observation[13] that the decrease in volume on freezing for the former is only half that for the latter. Therefore we do not even find appreciable changes of band envelopes or of positions of band

[10] H. K. Ward, J. Chem. Phys. **2**, 153 (1934).
[11] R. S. Rasmussen, reference 3.
[12] B. D. Saksena, Proc. Ind. Acad. Sci. **12A**, 321 (1940). The calculations reported in this paper have been checked by one of us; the value of 208 for the doubly degenerate ring distortion appears to be in error, the correct value being 330.
[13] D. Rozental, Bull. Soc. Chim. Belg. **45**, 585 (1936).

centers on freezing cyclohexane, whereas both types of changes were found in benzene (II).

One small difference between liquid and solid is observed: the band at 1350 wave numbers becomes somewhat narrower and deeper in the solid. This is probably one of the hydrogen modes, which we expect to be more strongly affected by slight changes in the molecular environment than the ring modes.

Two workers[14] have examined the Raman spectrum of solid I, but the slight changes which they report are not in sufficiently good agreement to permit much discussion.

Comparison of Solid I and Solid II

Since the effect of a large change in temperature is quite noticeable, it was necessary to repeat the measurement of the spectrum of solid I at a temperature just above the transition point (−87C) in order to be able to compare it with that of solid II just below the transition. The low temperature required in these observations (together with the increased resolving power of the spectrophotometer) causes the sharpening of the bands. We attribute to these factors alone the alterations produced in the appearance of the spectrum through the higher range of frequencies.

Here too the changes are slight, being found chiefly in the intensities of several bands. Most of the statements made in the preceding section concerning the similarity of structure and the slight changes of intermolecular forces accompanying the change of state are applicable here also.

An interesting feature of the spectra measured at low temperatures is that they show conclusively the presence of several shoulders and small bands, the existence of which was uncertain before: ~1022, ~1113, ~1266, ~2622, ~2675, ~2703, and ~2815.

The scarcity of developments accompanying condensation dissuades us from attempting any detailed analysis in terms of crystal structures. The spectra do indicate, however, that cyclohexane occupies in both solid forms a site[1] possessing a center of symmetry.

[14] S. M. Mitra, Phil. Mag. **25**, 895 (1938) and A. I. Siderova, Acta Physiochimica U. S. S. R. **7**, 193 (1937).

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Calculation of the Equilibrium Composition of Systems of Many Constituents[1]

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A computational procedure is developed for the calculation of the composition at chemical equilibrium of systems of many constituents. The general equations are applied to homogeneous systems and to homogeneous systems which exist in the presence of a single additional pure phase. A brief discussion is given of appropriate numerical methods of computation.

INTRODUCTION

THE calculation of the composition of a system at chemical equilibrium is easily carried out when there is only a single reaction to be considered. In this case, the concentrations of each constituent can be related to a single variable, "the degree of reaction," and the solution of the mass action equation is straightforward. Difficulties are encountered if this method is extended to a consideration of two simultaneous equilibria, and when the number of such simultaneous equilibria becomes large, the ordinary methods become very laborious.

There exists a need for a systematic procedure designed to provide a method for writing down the necessary relations in that form which is best suited to numerical computation. Such a procedure is developed in the present paper. Unfortunately, in order to achieve generality for the method, it has been necessary to adopt a somewhat complicated nomenclature. However, the reader who is not repelled by the analytical statement of the method will find its application to particular systems straightforward and the numerical solution of the resulting equations systematic. In an extensive program of computations, the author has employed clerical personnel in all numerical portions of the work.

CALCULATION OF THE EQUILIBRIUM COMPOSITION

In a recent discussion[3] of the conditions of equilibrium for systems of many constituents, it was shown that the number of components of a system containing s constituents is equal to the rank c of the matrix of the subscripts to the symbols of the elements in the formulae of the substances comprising the system. The choice of component substances must conform to the requirement that the vectors defined by the array of subscripts to the elementary symbols in the formulae of the selected substances be linearly independent. The substances, $s-c$ in number, with linearly dependent formula vectors may be considered to be formed from the components by the reactions,

$$\sum_{j=1}^{c} \nu_{ij} Y^{(j)} = Y^{(i)}, \tag{1}$$

$i=c+1, c+2, \cdots s$, where $Y^{(i)}$ and $Y^{(j)}$ represent the molecular formulae of the ith dependent substance and the jth component, respectively, and where ν_{ij} is the coefficient to the jth independent vector in the linear relation expressing the dependence of the ith dependent vector.

In terms of these definitions, the conditions of equilibrium assume a particularly symmetrical form. At constant temperature and pressure, the conditions for chemical equilibrium take the form,

$$\mu_j^{(k)} = \lambda_j, \tag{2}$$

$$\mu_i^{(k)} = \sum_{j=1}^{c} \nu_{ij} \lambda_j, \tag{3}$$

$k=1, 2, \cdots p$, $j=1, 2, \cdots c$, $i=c+1, c+2, \cdots s$, where $\mu_i^{(k)}$ and $\mu_j^{(k)}$ are the chemical potentials in the kth phase of the ith and jth substances, respectively, the λ_j are constants which may be eliminated from Eq. (2), p is the number of phases, and where it is assumed for simplicity of notation that each substance is included in every phase.

The conservation of mass in the system re-

[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior.
[2] Physical Chemist, Central Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pennsylvania.
[3] S. R. Brinkley, Jr., J. Chem. Phys. 14, 563 (1946).

quires that

$$\sum_{k=1}^{p} \{n_j^{(k)} + \sum_{i=c+1}^{s} \bar{\nu}_{ji} n_i^{(k)}\} = q_j, \quad (4)$$

$j=1, 2, \cdots c$, where $\bar{\nu}_{ji} = \nu_{ij}$ and where $n_i^{(k)}$ and $n_j^{(k)}$ are the number of gram moles in the kth phase of the ith and jth substances, respectively. The quantities q_j are obtained by solution of the linear equations,

$$\sum_{j=1}^{c} \bar{\alpha}_{lj} q_j = Q_l, \quad (5)$$

$l=1, 2\cdots$, where $\bar{\alpha}_{lj}$ is the subscript to the symbol of the lth element in the molecular formula of the jth component and Q_l is the number of gram atoms of the lth element available to the system.

Because of their symmetry, Eqs. (2)–(4) provide the simplest basis for the calculation of the composition of the system at equilibrium.

The chemical potential in the kth phase of the jth component is related to the mole fraction $N_j^{(k)}$ of the jth component in the kth phase by

$$\mu_j^{(k)} = [\mu_j^{(k)}]^0 + RT \log N_j^{(k)} f_j^{(k)}, \quad (6)$$

where

$$N_j^{(k)} = n_j^{(k)} / n^{(k)}, \quad (7)$$

$$n^{(k)} = \sum_{j=1}^{c} n_j^{(k)} + \sum_{i=c+1}^{s} n_i^{(k)}, \quad (8)$$

and where $f_j^{(k)}$ is the activity coefficient on the mole fraction concentration scale in the kth phase of the jth component, $[\mu_j^{(k)}]^0$ is the chemical potential of the jth component in the kth phase at the standard state of unit activity, and $n^{(k)}$ is the total number of moles in the kth phase. Similar definitions apply for the dependent substances.

A *representative phase* may be selected for each substance of the system. The representative phases for the jth component and ith dependent substance may be denoted, respectively, by the indices k_j and k_i. Introducing for simplicity, the abbreviations,

$$N_j^{(k_j)} = x_j, \quad N_i^{(k_i)} = x_i,$$

and employing the usual definitions and methods of thermodynamics, Eqs. (2), (3), and (6) lead to the relations,

$$N_j^{(k)} = a_{jk} x_j, \quad (9)$$

$$N_i^{(k)} = a_{ik} x_i, \quad (10)$$

$$x_i = b_i \prod_{j=1}^{c} x_j^{\nu_{ij}}, \quad (11)$$

$k=1, 2, \cdots p$, $j=1, 2, \cdots c$, $i=c+1, c+2, \cdots s$,

where

$$a_{jk} = K_j^{(k, k_j)} f_j^{(k_j)} / f_j^{(k)}, \quad (12)$$

$$b_i = K_i \prod_{j=1}^{c} [f_j^{(k_j)}]^{\nu_{ij}} / f_i^{(k_i)}. \quad (13)$$

It may be noted that $a_{jk}=1$ when $k=k_j$. If the jth substance is excluded *a priori* from the kth phase, then $a_{jk}=0$. The thermodynamic equilibrium constant $K_j^{(k, k_j)}$ for the distribution of the jth component between the kth and k_jth phases, is defined by

$$RT \log K_j^{(k, k_j)} = [\mu_j^{(k_j)}]^0 - [\mu_j^{(k)}]^0. \quad (14)$$

In a similar manner, a_{ik} is related to a distribution equilibrium constant for the ith dependent substance. The thermodynamic equilibrium constant K_i for the reaction

$$\sum_{j=1}^{c} \nu_{ij} [Y^{(j)}]_{k_j} = [Y^{(i)}]_{k_i},$$

is defined by

$$RT \log K_i = \sum_{j=1}^{c} \nu_{ij} [\mu_j^{(k_j)}]^0 - [\mu_i^{(k_i)}]^0. \quad (15)$$

If Eqs. (7) to (10) are combined with Eq. (4), there are obtained the relations,

$$q_j - x_j \sum_{k=1}^{p} a_{jk} n^{(k)} - \sum_{i=c+1}^{s} \bar{\nu}_{ji} x_i \sum_{k=1}^{p} a_{ik} n^{(k)}$$

$$= F_j(x_1, \cdots x_j, \cdots x_c; n^{(1)}, \cdots n^{(k)}, \cdots n^{(p)}) = 0, \quad (16)$$

$j=1, 2, \cdots c$. If Eqs. (9) and (10) are combined with the identity relations between mole fractions for each phase, there are obtained the additional relations,

$$1 - \sum_{j=1}^{c} x_j a_{jk} - \sum_{i=c+1}^{s} x_i a_{ik}$$

$$= G_k(x_1, \cdots x_j, \cdots x_c) = 0, \quad (17)$$

$k=1, 2, \cdots p$. In view of the relations between the x_i and the x_j which are expressed by Eqs. (11), Eqs. (16) and (17) consist of $c+p$ relations between the variables $x_1, x_2, \cdots x_c, n^{(1)}, n^{(2)}, \cdots n^{(p)}$. If these equations can be solved simultaneously, the complete solution for the composition of the system can then be obtained at once by the use of Eqs. (9) to (11).

It is not usually feasible to seek a literal solution of these equations, and it is, therefore, necessary to employ an iterative procedure. As a first approximation, Eqs. (16) and (17) are solved with neglect of the dependence of the activity coefficients on the composition, and the quantities a_{jk}, a_{ik}, and b_i are evaluated either with activity coefficients corresponding to approximate values of the concentrations of the several constituents, or, in the absence of such information, with activity coefficients set equal to unity corresponding to the assumption that the phases are ideal. The results of the first approximate solution are then used to evaluate improved values of the coefficients, and these in turn are employed in a second solution of Eqs. (16) and (17) to obtain second approximate values of the concentrations. This process, which may be called the *primary iteration*, is continued until the difference between successive approximations to every variable is negligibly small. If the phases may be considered to be ideal, the primary iteration reduces to a single step.

In each step of the primary iteration, the solution of Eqs. (16) and (17) must be obtained by a series of successive approximations, which may be called the *secondary iteration*. The Newton-Raphson[4] method is well suited to this stage of the calculation. If the functions F_j and G_k are expanded in a Taylor series about an approximate set of values of the variables with neglect of terms involving derivatives of second and higher orders, there results a set of $c+p$ linear equations which can be compactly represented in the notation of matrices by

$$\left[\begin{array}{c|c} A_{jj'}{}^{(r)} & B_{jk'}{}^{(r)} \\ \hline \bar{B}_{kj'} & 0 \end{array}\right]\left[\begin{array}{c} h_{j'}{}^{(r)} \\ \hline g_{k'}{}^{(r)} \end{array}\right]=\left[\begin{array}{c} F_j{}^{(r)} \\ \hline G_k{}^{(r)} \end{array}\right], \quad (18)$$

where the rth and $(r+1)$th approximations to the composition are related by

$$x_j{}^{(r+1)}=x_j{}^{(r)}(1+h_j{}^{(r)}),$$

$$[n^{(k)}]^{(r+1)}=[n^{(k)}]^{(r)}+g_k{}^{(r)},$$

and where the elements of the submatrices are given by

$$A_{jj'}=x_j\delta_{jj'}\sum_{k=1}^{p}a_{jk}n^{(k)} + \sum_{i=c+1}^{s}\bar{\nu}_{ji}\bar{\nu}_{j'i}x_i\sum_{k=1}^{p}a_{ik}n^{(k)}, \quad (19)$$

$$B_{jk}=x_ja_{jk}+\sum_{i=c+1}^{s}\bar{\nu}_{ji}x_ia_{ik}, \quad B_{kj}=B_{jk}, \quad (20)$$

$k, k'=1, 2, \cdots p$, $j, j'=1, 2, \cdots c$. The x_i are related to the x_j by Eqs. (11), and $\delta_{jj'}$ is the Kronecker delta. The functions F_j and G_k are defined by Eqs. (16) and (17), and the superscript r indicates that the quantity to which it refers is to be evaluated with the rth approximation to the composition of the system.

Two examples will suffice to illustrate the application of Eqs. (18) to particular systems. If the system exists in a single phase, the elements of the submatrix $A_{jj'}$ are given by

$$A_{jj'}=n_j\delta_{jj'}+\sum_{i=c+1}^{s}\bar{\nu}_{ji}\bar{\nu}_{j'i}n_i, \quad (21)$$

and the submatrices B_{jk} and $\bar{B}_{kj}$ become column and row matrices, respectively, with elements

$$B_j=\bar{B}_j=N_j+\sum_{i=c+1}^{s}\bar{\nu}_{ji}N_i. \quad (22)$$

If component $Y^{(1)}$ exists in a pure phase which is designated by the index σ and not in any other phase, and if all other constituents exist in a single phase designated by the index γ then $G_\sigma{}^{(r)}=0$ for every r and it is easy to show by the combination of rows of the augmented matrix that Eqs. (18) for this case reduce to $h_1{}^{(r)}=0$ for every r, and

$$\begin{bmatrix} A_{1j'}{}^{(r)} & 0 & 1 \\ A_{jj'}{}^{(r)} & B_{j\gamma}{}^{(r)} & 0 \\ \bar{B}_{\gamma j'}{}^{(r)} & 0 & 0 \end{bmatrix}\begin{bmatrix} h_{j'}{}^{(r)} \\ g_\gamma{}^{(r)} \\ g_\sigma{}^{(r)} \end{bmatrix}=\begin{bmatrix} F_1{}^{(r)} \\ F_j{}^{(r)} \\ G_\gamma{}^{(r)} \end{bmatrix}, \quad (23)$$

$j, j'=2, 3, \cdots c$. The matrix elements may be found from Eqs. (19) and (20) with the substitu-

[4] J. B. Scarborough, *Numerical Mathematical Analysis* (The Johns Hopkins Press, Baltimore, 1930), pp. 178, 187.

tions, $a_{1\sigma}=a_{j\gamma}=a_{i\gamma}=1$, $a_{1\gamma}=a_{j\sigma}=a_{i\sigma}=0$. If component $Y^{(1)}$ is present in unlimited excess, then $F_1=\infty$. In this case, Eqs. (23) may be written in the form,

$$\begin{bmatrix} A_{jj'}{}^{(r)} & B_{j\gamma}{}^{(r)} \\ \bar{B}_{\gamma j'}{}^{(r)} & 0 \end{bmatrix} \begin{bmatrix} h_{j'}{}^{(r)} \\ g_{\gamma}{}^{(r)} \end{bmatrix} = \begin{bmatrix} F_j{}^{(r)} \\ G_{\gamma}{}^{(r)} \end{bmatrix}. \quad (24)$$

DISCUSSION

Criteria for that choice of components and representative phases which results in the most rapid convergence of the secondary iteration can be developed from the remainders to the two-term Taylor series expansions of the functions F_j and G_k. However, the resulting expressions are too cumbersome for practical utility, and in practice the convergence will be found to be satisfactory if representative phases are selected so as to minimize the sets of quantities a_{jk} and a_{ik}, $k=1, 2, \cdots p$, for each i and j, and if the components are selected so as to minimize the set of quantities b_i, $i=c+1, c+2, \cdots s$.

Equations (18) are conveniently solved by matrix methods, of which that of Crout[5] is particularly well adapted to machine computation. When, at some stage in the secondary iteration, the residuals $F_j{}^{(r)}$ and $G_k{}^{(r)}$ become fairly small, an appreciable saving of time results if the coefficients $A_{jj'}{}^{(r)}$, $B_{jk'}{}^{(r)}$ and $\bar{B}_{kj'}{}^{(r)}$ are retained for all subsequent steps in the iteration.[6] Although the number of steps remaining is thereby increased, the amount of computation in each step is greatly reduced, particularly if the Crout method of reduction of the matrix is employed. When some of the a_{jk}, a_{ik}, or b_i are much larger than the others, it is frequently advantageous to obtain a preliminary solution of Eqs. (18) with neglect of the coefficients which are relatively small. The solution can then be completed in the manner indicated above with constant values of the elements of the square matrix.

[5] P. D. Crout, Trans. A.I.E.E. **60**, 1235 (1941).

[6] E. T. Whittaker and G. Robinson, *The Calculus of Observations* (Blackie and Son, Ltd., London and Glasgow, 1929), second edition, p. 90.

Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

A Simplified Method of Calculating Absorbed Intensity in Photometric Experiments

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January 10, 1947

IN studying photochemical reactions it is frequently necessary to calculate the intensity of absorbed radiation from measurements of the transmitted intensity. The usual method is an approximate one and involves calculation of the fraction of light reflected and re-reflected from each interface of the cell windows, and then the amount of this reflected radiation actually absorbed by the gas in question. These corrections are continued until the desired degree of accuracy is obtained. Much of the tedious computation may be avoided by using instead a treatment which is exact within the limits of the assumptions made.

Let us assume that a parallel beam of light is incident upon the front (optically plane) window of a reaction vessel and that it passes through the vessel and out the rear window where it is then completely captured by a photo-cell, thermopile or actinometer. Examining for the moment of a single window, a certain fraction (f) of the light incident upon any interface will be reflected. A certain small fraction will be absorbed by the window itself and lost. This may be combined with the fraction lost due to scattering by the surface and by imperfections in the window itself, and the total represented by w. The situation then for each window is shown in Fig. 1. Summing up the two infinite series representing total radiation reflected (R) and transmitted (T), and putting them in the form $1/1-x$, we obtain

$$R=f+\frac{(1-f)^2f(1-w)^2}{1-(1-w)^2f^2}, \tag{1}$$

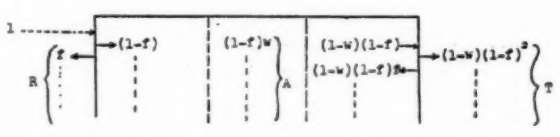

FIG. 1. Radiation reflected, absorbed, and transmitted by a single window.

$$T=\frac{(1-w)(1-f)^2}{1-(1-w)^2f^2}. \tag{2}$$

Also, $R+T+A=1$, where A is the total radiation absorbed and scattered.

We now consider the cell as a whole, with two such windows separated by a column of absorbing gas. Let α be the fraction of radiation which is absorbed in a single passage through the gas column. Let us assume also that the windows are identical in behavior. This situation may be pictured as in Fig. 2. Again summing separately the terms representing radiation reflected from the front of the cell, absorption by the gas column, and radiation transmitted at the rear of the cell, we obtain in a similar manner

$$\frac{I_a}{I_0}=\frac{T\alpha}{1-R(1-\alpha)}, \tag{3}$$

$$\frac{I_t}{I_0}=\frac{T^2(1-\alpha)}{1-(1-\alpha^2)R^2}. \tag{4}$$

Here I_a and I_t are the absorbed (by the gas) and transmitted intensities, and I_0 is the incident intensity striking the front window. With the cell evacuated, α in Eq. (4) becomes zero, yielding a relation between incident intensity and that transmitted by the empty cell (I_t^0):

$$I_t^0/I_0=T^2/(1-R^2). \tag{5}$$

T, R, and w may then be found from Eqs. (1), (2), and (5), using a value of f calculated from Fresnel's law for reflection at an interface, and inserting the measured values of I_0 and I_t^0. For a good grade of fused quartz and an evacuated cell ($f=0.038$), the values of R and T turn out to be about 0.07 and 0.91, respectively, and w comes out somewhat smaller than f.

The complete procedure in principle is the following: calculate R, T, and w as indicated above; then employing these values of R and T and an experimental value of I_t/I_0, α is found from Eq. (4); finally, α, R, and T are substituted into Eq. (3) to give I_a/I_0. However, in practice, we may neglect, to a good approximation (about 0.5 percent, or less), R^2 and f^2 compared to unity in Eqs. (1), (2), (4), and (5), and obtain

$$R=f+(1-f)^2f(1-w)^2, \tag{1'}$$

$$T=(1-w)(1-f)^2, \tag{2'}$$

$$I_t/I_0=T^2(1-\alpha), \tag{4'}$$

$$I_t^0/I_0=T^2. \tag{5'}$$

These simplified equations may now easily be combined to give α, R, and T as explicit functions of the experimental quantities f, I_t/I_0, and I_t^0/I_0. Substituting these expressions for α, R, and T into Eq. (3), we have the final result

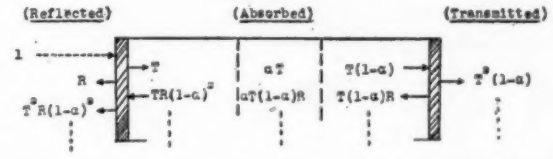

FIG. 2. Radiation reflected, absorbed, and transmitted by a cell with plane parallel windows, which contains a substance absorbing (in a single passage) a fraction α of the light incident upon it.

$$\frac{I_a}{I_0}=[(I_t^0/I_0)-(I_t/I_0)]\times\frac{(I_t^0/I_0)^4}{(I_t^0/I_0)-f\left[1+\frac{(I_t^0/I_0)}{(1-f)^2}\right](I_t/I_0)}. \quad (6)$$

It might be pointed out that a method sometimes used in spectrophotometric work for calculating the absorbed intensity—namely, taking the simple difference between transmitted intensity with the cell empty and filled with gas—can introduce a large error. The factor multiplying $(I_t^0/I_0)-(I_t/I_0)$ in Eq. (6), in a typical case (i.e., $I_t^0/I_0=0.85$, $f=0.04$), varies from 1.08 for complete absorption by the gas to 1.17 at zero absorption.

We have referred throughout to absorption by a gas. It is clear that a very similar treatment can be given for a liquid solution.

Polarization of Raman Lines

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IN earlier studies of the polarization of Raman lines[1-3] we suggested certain arrangements of polaroid films in front of the slit of the spectrograph. At that time we also employed grids to obtain nearly parallel incident light, in order to measure the depolarization factor. In many experiments on the Raman effect it is, however, sufficient to know which of the Raman lines are depolarized without necessarily determining the depolarization factor numerically. We have therefore evolved another experimental set-up as shown in Fig. 1.

Two Raman tubes (*Ra*) are supported by two brass tubes (*B*). These brass tubes carry on the other end two condensing lenses (*Le*). The bottom of the top Raman tube and the top of the bottom Raman tube are both painted with a strip of optical black ($\frac{1}{8}$" wide) and parallel to the Raman tube axis. This black strip avoids scattered radiation from each Raman tube interferring with the other. The scattered radiation coming through the windows of the Raman tubes is focused by means of the two lenses (*Le*) (focal length 12.2 cm) onto the slit of the spectrograph. An appropriate diaphragm is placed in front of the slit and the two scattered beams are separated by a blackened metal foil. The distance between the Raman windows and the lenses is 15.3 cm and the distance from the lenses to the double slit is 17.9 cm.[4] The brass tubes (*B*) are adjusted by six screws each, until the two scattered light beams from the Raman tubes have the same intensity and shape of image when viewed in the spectrograph. One of the Raman tubes is surrounded by a film of polaroid in which the electric vector lies along the axis of the Raman tube, whereas the second Raman tube is wrapped in a piece of polaroid with its electric vector at right angles to the axis of the Raman tube. We used twelve A. H. 2 General Electric Company mercury vapor lamps arranged horizontally in circular fashion, surrounded by a silvered cylindrical metal reflector. This arrangement is somewhat similar to one described by Edsall and Wilson.[5] Between the Raman tubes and the mercury lamps there is located a water jacket which keeps the heat generated by the lamps from reaching the substance under investigation. The mercury lamps are kept at constant temperature by using a bi-metallic temperature control. Its mercury switch operates the motor of a blower which draws air past the lamps, cooling them. This control is intermittent, but works very satisfactorily. Another blower draws air through the inner region of the water jacket, containing the Raman tubes. By adjusting the speed of this motor, the temperature of the inner region is kept remarkably constant.

We obtain the spectrum of carbon tetrachloride with polaroid films as shown in Fig. 2. With the above-mentioned light sources, the photograph could be taken in four hours' exposure. It is not necessary to use filters. The photographic plates employed were Eastman Kodak 103a-0. By surrounding the two Raman tubes with an appropriate system of metal grids, it should be possible to make the incident light parallel. A numerical measure of the depolarization factor could then be obtained.

An advantage of the new arrangement lies in the fact that current fluctuations affect both Raman tubes in the same way. The qualitative results obtained are sufficient to indicate the depolarized lines.

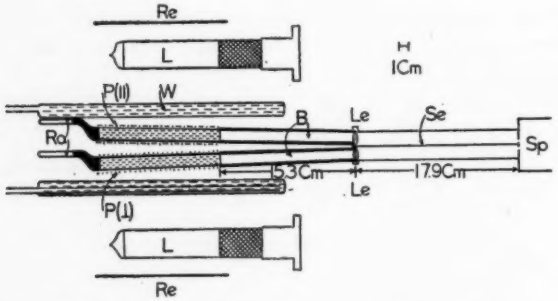

FIG. 1. Raman apparatus. *Re*=reflector, *L*=lamps, *W*=water jacket, *Ra*=Raman tubes, *P*(II), *P*(⊥)=polaroid films, *B*=brass tubes, *Le*=condensing lenses, *Se*=separating blackened metal sheet, *Sp*=spectrograph.

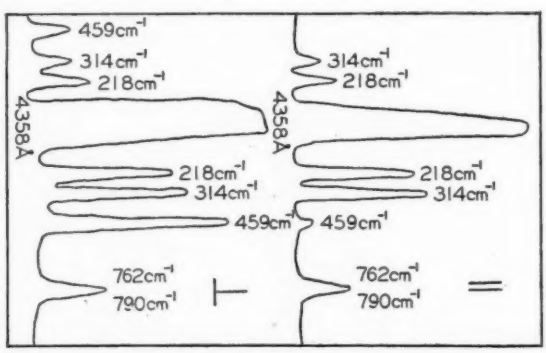

FIG. 2. Microphotograph of CCl_4 spectrum.

We wish to thank Professor B. L. Crawford of the University of Minnesota for the microphotograph (Fig. 2), and the China Institute in America for financial support to one of us (J. Y. T.).

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Note on a Proposed Interpretation of the Zeta-Potential

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THE graph of zeta-potential *vs.* concentration in a recent article by this writer[1] should have had the ordinate marked *minus zeta-potential* rather than *zeta-potential* as was shown. It is hoped that this error did not lead to confusion. Examination of the original data would have shown that the zeta-potentials of potassium chloride and barium chloride are negative.

Attention also should be called to another aspect of the new definition of the zeta-potential. Calculations already made by Jones and Wood[2] and Wood and Robinson[3] have shown that Langmuir's theory of the *Jones-Ray Effect* was strikingly substantiated. These calculations were based on the conventional Helmholtz-Perrin values of the ζ-potential. When these corrected surface tensions are recalculated on the basis of the newly defined zeta-potential, no difference in the previous results is obtained (for potassium chloride and barium chloride). The curves given by Jones and Frizzell[4] and Wood and Robinson[3] show that the wetting film thicknesses approach some definite value as the potential increases. The experimental values of the zeta-potential determined in the conventional manner are sufficiently large to be on the part of the curve where further increases in the potential have little or no effect on the thickness of the wetting film. Consequently, the newly defined zeta-potential leaves the corrected values of the surface tension just as they were found from the Helmholtz-Perrin zeta-potentials.

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On the Equation of State for Gases at Extremely High Pressure*

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IN an article bearing the above title, Caldirola[1] has employed the hydrodynamic theory of stationary detonation waves, with experimental values of the detonation velocity, to determine an equation of state valid for the high pressures and temperatures characteristic of the detonation process. The treatment is based upon the Rankine,[2] Hugoniot[3] equations for the continuity of mass, momentum, and energy across the detonation front and the Chapman[4]-Jouget[5] condition for the stable detonation state. The specific-energy increment accompanying the detonation reaction is computed by the thermodynamic relation,

$$E=\bar{C}(T-T_0)-q, \tag{1}$$

where $\bar{C}$ is the mean specific heat of the detonation products and q the specific heat of reaction at constant volume and at temperature T_0. The equation of state is assumed to be of the form,

$$pv=r(v)T. \tag{2}$$

We note that Caldirola's calculated values of the detonation temperature increase with increasing density of the explosive.

The writer does not feel that this equation of state is of sufficiently general form for application to the products of detonation of solid explosives, since it implies that the gaseous products are thermodynamically ideal,

$$(\partial E/\partial v)_T=0.$$

Hirschfelder and his associates[6-7] have pointed out that the internal energy of a gas is a linear function of its density to moderate pressures,

$$E=E_0(T)-\frac{RT^2}{V}\frac{dB(T)}{dT}, \tag{3}$$

where $B(T)$ is the second virial coefficient, and tables have been provided[7] that permit evaluation of the energy of gas imperfection for substances to which the Lennard-Jones intermolecular potential-energy function applies. The contribution of the second virial coefficient to the energy of gas imperfection is negative at low temperatures and positive for temperatures greater than that for which Em/kT is equal to about 0.04 (Em is the maximum energy of attraction between a pair of molecules). An estimate, based on Eq. (3) and the molecular constants listed by Hirschfelder,[6] leads to a positive value of about 2 kcal./mole for the energy of gas imperfection of CO at 4500°K and density of 1.5. This figure is not negligible in comparison with the temperature-dependent part of the internal energy at zero density and the same temperature, 29 kcal./mole.[8] At the same temperature and density, the second virial coefficient contributes to the internal energies of H_2 and CO_2 of about $+1.2$ kcal./mole and -0.3 kcal./mole, respectively. At high density, terms in higher powers of the density would become significant through the contributions of the third and higher virial coefficients, and one would expect the internal energy to increase exponentially with the density.[6]

From these considerations, it would appear that Eqs. (1) and (2) should be replaced by

$$E=\bar{C}(T-T_0)-q+\int_\infty^V\left[T\left(\frac{\partial p}{\partial T}\right)_V-p\right]dv, \tag{1'}$$

$$pv=r(v, T)T, \tag{2'}$$

respectively. Rough calculations indicate that the detonation temperature decreases with increasing density of the explosive when the energy of gas imperfection is taken into account. It is unfortunate that, when Eqs. (1′) and (2′) are employed with the hydrodynamic equations, the ingenious method of Caldirola for determining the equation of state is inapplicable, since evaluation of the integral of Eq. (1′) will involve some assumption as to the form of the function $r(v, T)$ for all values of the density from zero to its detonation value.

These considerations are based in part upon work in progress in this laboratory on the equation of state for detonation products of solid explosives. This work is supported from funds derived from the Office of Naval Research for studies of the physics and chemistry of explosive phenomena, and it will be reported upon at a later date.

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